

Conformational properties of trimethyl phosphate monomer

Igor Reva *, Alcides Simão, Rui Fausto

Departamento de Química, Universidade de Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

Received 29 January 2005; in final form 17 February 2005

Available online 17 March 2005

Abstract

Conformational isomerism of trimethylphosphate (TMP) has been studied de novo. TMP monomers were isolated in low temperature xenon matrices at different substrate temperatures and characterized using FTIR spectroscopy. At the lowest temperature, three different conformers, with overall molecular symmetries C_3 , C_1 and C_s , were shown to co-exist in the matrix. Increase of the sample temperature led to conformational cooling, with the two minor conformers being depopulated successively, following an order of increasing stability. Initially, the less stable C_s conformer converted to the C_1 form and, at higher temperatures, the C_1 conformer converted to the global energy minimum, C_3 . Interpretation of the experimental data was supported by extensive calculations of the vibrational spectra and barriers to the conformational interconversion.

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1. Introduction

One of the first accounts on the trimethyl ester of orthophosphoric acid, $PO_4(CH_3)_3$, relates to the 19th century [1]. In 1883, Weger determined its boiling point [1] to be 197.2 °C (and this value is accepted unaltered nowadays). Still in the 19th century, Cavalier studied again its physical properties and reported [2] that the compound has a pleasant smell. A few decades later, this pleasant smell was specified as buttery [3]. Much later, it has been recognized that trimethyl phosphate (TMP) possesses mutagenic activity [4,5]. TMP is well known as a model compound stably reproducing animal male sterility effect [6]. High mutagenic and pathogenic activity of TMP might be the result of its high conformational flexibility.

In one of the early conformational studies Raevskii et al. [7] constructed 16 different conformations of the $(CH_3-O)_3-P=O$ molecule, by varying the angles of rotation around the three P–O bonds (assuming values of 0°,

120°, 180° and 240°). Even after discarding several sterically crowded geometries, many structures still remained good candidates for minimum energy conformations. In fact, the problem of conformational isomerism in TMP has been addressed many times during several decades. The molecule has been extensively studied in the past using vibrational spectroscopy in solutions [7–19], in gaseous [18,20] and solid [17–19] phases, and isolated in cryogenic matrices [19–24]; NMR spectroscopy [14,15,25]; electron diffraction [26]; dipole moments and Kerr constants methods [7,27]; dielectric loss spectroscopy [28]; and theoretically [14,21,29–31]. And this big list of references is far from being complete.

The majority of the conformational studies on TMP demonstrated the existence of the TMP molecule in two stable conformations. However, the reported structures were very controversial. The structures of possible conformers are usually addressed in terms of their overall symmetry (C_{3v} , C_3 , C_s and C_1). In 1957, Mortimer observed [10] the splitting of the P=O stretching band in the infrared spectra of liquid TMP. He explained this fact in terms of more than one rotational isomer. Practically, all subsequent experimental studies observed doublets in the spectra of liquid TMP or its solutions,

* Corresponding author. Fax: +351 239 827 703.

E-mail address: reva@qui.uc.pt (I. Reva).

the splitting being systematically interpreted in terms of conformational multiplicity. In the discussion of the vibrational assignments, Mortimer considered the symmetry of both isomers to be at least approximately C_3 (one of them being C_{3v}) [10]. The assumption of existence of a threefold symmetry axis appeared in many subsequent studies [20,25–27]. However, in other works [30,31] it was duly noticed that there is no reason to assume that phosphate structures exhibit any overall symmetry. Indeed, experimental studies could not confirm [18] or had excluded [32] the possibility of occurrence of the TMP molecule in a conformation with the C_{3v} symmetry. Streck et al. [9] also noticed that ‘*the splittings observed for the C–O antisymmetric stretching, PO_3 antisymmetric stretching and PO_3 antisymmetric deformation modes originate in part from the presence of two conformers. However, in these regions the degeneracy of the modes is lifted in the lower symmetry conformer(s) and thus two bands are observed even under conditions in which the C_3 symmetry conformer is absent*’.

Summarizing the latest conformational findings, it can be said that TMP adopts in condensed media two conformations, C_3 and C_1 . It has been experimentally observed that changes of the electric properties of the medium strongly influence the conformational equilibrium in TMP [7–9]. In weakly polar solvents, the most stable form corresponds to the C_3 symmetry conformer. In solvents of higher polarity, the reversal occurs and the C_1 conformer, having higher dipole moment, becomes the most stable form. Finally, there are also vague indications for the possible existence of a third conformer, C_s . In particular, two Raman studies [14,17] refer to the experimental observation of three rotational isomers of TMP (C_3 , C_s and C_1) in the liquid state. However, it should be noted that the assignment of the unique signals due to the C_s form in the experimental spectra seems extremely difficult. In the work of Taga et al. [17], the presence of the C_s form is justified by the observation in the liquid phase spectrum of TMP of one, very weak shoulder-band at 440 cm^{-1} . All the remaining signals that could result from the C_s form, are always accompanied by signals due to other (C_3 and/or C_1) conformers [14,17].

Theoretical calculations performed at the STO-3G* and 4-31G* levels of theory [30] predicted the C_1 form as the most stable. On the other hand, the semi-empirical AM1 method predicted the energy of the three conformers as increasing in the order $C_s < C_1 < C_3$ [23]. Higher level HF/6-31G** and MP2/6-31G** ab initio computations [23,31], however, yielded a different energy order for the three conformers: $C_3 < C_1 < C_s$. In a recent theoretical study performed at the HF/PM3 level [14], the two-dimensional potential energy hyper-surface of TMP was calculated. Two O=P–O–C dihedral angles were varied, while the third was fixed at 42° . The most stable form was not specified, but it was found that sev-

eral conformers with different symmetry (C_3 , C_1 or C_s) were lying in a restricted energy range. This fact would explain diversity and contradictions between theoretical and experimental results reported in the literature.

Among the previously reported conformational studies of TMP, those undertaken by matrix isolation spectroscopy [19–23] are specially relevant from the viewpoint of the present Letter. Matrix isolation data indicated that, in the gaseous phase, TMP should exist in two stable conformations. In early matrix works [19,20,22] there were some discrepancies regarding the nature of the observed conformers. But in the follow-up publications [23,31] it was concluded that only the C_3 and C_1 conformations would have significant population to be experimentally important. Vidya et al. [22] studied the conformational cooling of TMP monomers isolated in matrices of argon and nitrogen. They found that in the temperature range up to 35 K it was impossible to populate selectively only the lower energy conformer. Supersonic expansion has been used to achieve cooling in the gas phase and the higher energy conformer was significantly depopulated prior to deposition [22]. Subsequent theoretical analysis [31] showed that it was the C_3 form which dominated in matrices after supersonic jet cooling. The same theoretical work [31] showed that the barrier for conversion of the C_1 conformer into the C_3 form was equal to 2.2 kcal mol^{-1} . This barrier was high enough to prevent depopulation of the C_1 form in argon and nitrogen matrices where TMP was deposited using effusive source (hot nozzle technique). The possibility of observation of the third conformer, C_s , was discarded in the previous matrix studies and barriers separating this conformer from the other forms were not considered.

In our recent Letter of cyanoacetic acid and methyl cyanoacetate isolated in low temperature inert matrices [33] we addressed properties of different matrix gas hosts from the viewpoint of conformational cooling. We have shown that in the series argon–krypton–xenon, xenon has the best relaxant properties. Usage of xenon as the matrix host allowed us to observe efficient conformational cooling of methyl cyanoacetate monomers, while with argon as the matrix host the conformational cooling of methyl cyanoacetate was extremely difficult to achieve [33]. By analogy with our previous work, where the studied compounds were deposited with an effusive source [33], one could expect that usage of xenon as the matrix host could also promote conformational cooling in TMP. We explored this idea in the present Letter.

2. Experimental methods and calculations

Commercial trimethyl phosphate (99+%, Aldrich) was used in the present Letter. Due to the pathogenic

activity of TMP, all treatment of the samples was performed in a glove-box, in order to prevent inhalation of vapors of the compound. Besides that, the glove box was purged with dry nitrogen, in order not to expose the compound to the atmospheric water. Argon N60 and xenon N45 (Air Liquide) were used without further purification. The low-temperature equipment was based on a closed-cycle helium refrigerator (APD Cryogenics) with a DE-202A expander. Infrared spectra were registered with resolution of 0.5 cm^{-1} , in the range $4000\text{--}400\text{ cm}^{-1}$, using a Mattson (Infinity 60AR Series) Fourier transform infrared spectrometer equipped with a DTGS detector and a Ge/KBr beam-splitter. An effusive Knudsen cell with a SS-4BMRG (NUPRO) needle valve was used to sublime TMP. Prior to experiment, the compound was additionally purified from dissolved gases by pumping through the cryostat. Before deposition, TMP was cooled to $-79\text{ }^{\circ}\text{C}$ (ca. 23° below its melting point) by immersing the ampoule with the compound into a Dewar vessel with melting 1-pentanol. This allowed reducing the saturated vapor pressure over the solid TMP and improving the metering function of the valve. The valve nozzle was kept at room temperature (295 K) and this temperature defined the conformational populations of the compound before deposition. The deposition rate of TMP was chosen low enough to ensure that the species trapped in matrices were mainly monomers. A CsI window was used as the optical substrate for matrices. Temperature was measured directly at the sample holder by a silicon diode sensor connected to a digital controller (Scientific Instruments, Model 9650-1), with accuracy of 0.1 K.

The equilibrium geometries of the low energy conformers of TMP were fully optimized using the TIGHT criteria at the DFT(B3LYP) and MP2 levels of theory with the standard 6-31G(d,p), 6-31++G(d,p), 6-311++G(d,p) and 6-311++G(2d,2p) basis sets. Where applicable, calculations were performed with the explicit usage of symmetry. Optimizations were followed by frequency calculations, which were also used to check the nature of calculated stationary points. Both MP2 and DFT methods were used to obtain the reaction pathways for conformational interconversion and to locate the transition states. The best correspondence between the theoretical and experimental spectra was obtained in the case of the DFT(B3LYP)/6-311++G(2d,2p) calculations and xenon matrices. In the fingerprint region there were over- and under-estimated frequencies, the mean square deviation being 1.2%, and the average scaling factor being equal to unity! All calculations were done using the GAUSSIAN 98 program [34] (Gaussian, Inc.). Molecule vibrations were visualized using the GAUSSVIEW 2.1 for Windows (Gaussian, Inc.).

3. Results and discussion

3.1. Theoretical calculations

The molecule of TMP has three internal axes of freedom, which correspond to rotation of the methyl groups around the O–P bonds. These internal rotations can result in occurrence of several conformers. In conformity with previous works, we adopted the names of the conformers accordingly with their overall symmetry. The three additional internal degrees of freedom, corresponding to rotation of the methyl groups around the C–O bonds, do not produce additional conformers and will not be addressed further. The three possible conformers of TMP and their symmetries are shown in Fig. 1. The values of the three O=P–O–C dihedral angles characterizing each TMP conformer as well as their calculated energies are summarized in Table 1. It is obvious from

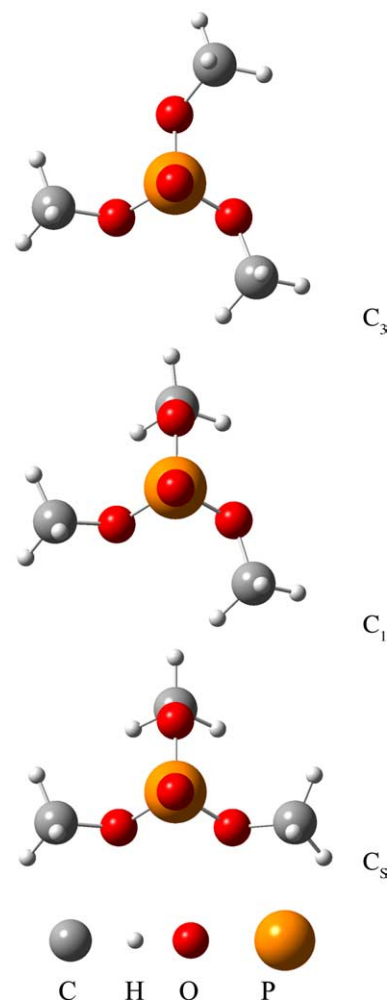


Fig. 1. Optimized geometries of trimethyl phosphate, $\text{O}=\text{P}-(\text{O}-\text{CH}_3)_3$. Conformers are named according to their overall symmetry. The viewpoint is chosen in such a way that the $\text{P}=\text{O}$ bond is perpendicular to the plane of the figure and the phosphorous atom is eclipsed by the oxygen ($\text{O}=\text{O}$). Element codes are given in the lowest row.

Table 1

Calculated energies (E^a), equilibrium populations (P^d), dipole moments (D^e), electronic spatial extents (S^f) and optimized values of the three O=P–O–C dihedral angles (A^j) of trimethyl phosphate conformers

Calculation method	Value	Conformation		
		C ₃	C ₁	C _s
B3LYP/6-31G(d,p)	E	–761.926273	3.6	7.5
	P	56.8	39.2	4.0
	D	0.7	3.6	2.8
	S	1145.6	1113.8	1126.8
	A	44.0	33.9; 178.2; 53.1	33.2
B3LYP/6-311++G(d,p) ^b	E	–762.075365	3.1	9.0
	P	53.0	45.0	2.0
	D	1.0	3.9	3.0
	S	1157.8	1126.9	1139.7
	A	44.4	33.5; 177.3; 53.1	31.4
B3LYP/6-311++G(2d,2p)	E	–762.112868	4.3	8.2
	P	63.6	33.0	3.4
	D	0.9	3.7	3.1
	S	1140.5	1110.8	1117.3
	A	42.5	35.8; 178.5; 49.2	38.4
MP2/6-31G(d,p)	E	–760.237284	2.6	6.0
	P	46.1	47.9	6.0
	D	0.6	4.2	3.3
	S	1133.2	1099.3	1108.3
	A	45.0	37.0; 177.9; 55.4	39.9
MP2/6-31++G(d,p)	E	–760.270770	1.6	6.5
	P	37.5	58.5	4.0
	D	0.9	4.3	3.6
	S	1144.5	1110.2	1116.3
	A	44.8	37.2; 178.3; 54.2	41.7
MP2/6-311++G(d,p) ^c	E	–760.600799	1.5	9.3
	P	37.6	61.1	1.3
	D	1.0	4.3	3.4
	S	1136.0	1103.9	1112.3
	A	46.8	37.1; 177.2; 55.4	39.2
MP2/6-311++G(2d,2p) ^c	E	–760.747647	2.7	6.5
	P	47.5	47.5	5.0
	D	0.9	4.0	3.6
	S	1123.8	1092.1	1094.1
	A	43.8	39.1; 177.8; 50.5	44.4

^a E : Absolute energies for the C₃ form (global minimum at all presented levels) are given in Hartrees, relative energies for the C₁ and C_s forms are given in kJ mol^{–1}. The zero-point vibrational energy (ZPVE) contribution is included.

^b At this level, no minimum could be located for the C_s conformer either with or without symmetry. One imaginary frequency (ca. 7 (i) cm^{–1}) was always present. Thus one lowest frequency was excluded from the ZPVE for all forms at this level.

^c Frequency calculations were not performed at these levels. Energies do not include ZPVE in these cases.

^d P : Equilibrium populations in %, at 295 K. Degeneracy of states was taken as 2, 6 and 3 for the C₃, C₁ and C_s, respectively.

^e D : Molecular dipole moments in Debye.

^f S : Electronic spatial extents in arbitrary units.

^j A : Dihedral angles in degrees. For the C₃ form all dihedral angles are equal by symmetry and have the same value and sign. For the C_s form one of the dihedral angles is equal to 180° by symmetry, whereas the other two dihedral angles are equal by absolute value (presented in the table) and have opposite sign.

this table that the dihedral angles do not vary significantly for the structures optimized at different theory levels. The same observation applies to the calculated relative energies. The C₃ form is predicted as the most stable at all theory levels; it is followed by the C₁ form, whereas the less stable conformer is the C_s form.

In earlier experimental studies reporting the relative stabilities of the C₃ and C₁ forms [9,18], this conclusion

was based on the change of the relative intensities of the signals ascribed to the individual conformers with the change of temperature. In such approach, degeneracy of conformational states is irrelevant. However, it should be kept in mind that a less stable form can have higher population in the equilibrium mixture with respect to the most stable form, if it has a higher degeneracy. This is exactly the case of TMP. None of previous

studies, however, has addressed the issue of degeneracy of the TMP conformers. The lowest symmetry conformer, C_1 , has the highest degeneracy, which is equal to 6: each TMP molecule has three methyl groups, any of them can have *trans* orientation and, for each *trans* orientation, the remaining two methyl groups can be oriented clockwise or counter-clockwise with respect to the O=P axis. The highest symmetry form, C_3 , has the lowest degeneracy, which is equal to 2 (clockwise or counter-clockwise orientation of the methyl groups with respect to the O=P axis; these two forms are mirror images). Finally, the C_s conformer has degeneracy 3: for each *trans* methyl group the remaining two CH_3 groups have a unique orientation (see Fig. 1). It can be seen from Table 1 that, if the energy gap between the C_1 and C_3 forms is low enough (like predicted by all MP2 calculations – less than 3 kJ mol^{-1}), then the highly degenerated C_1 form dominates in the equilibrium, even at room temperature. What is more important is the fact that the theoretically predicted population of the C_s form in the equilibrium mixture at room temperature ranges from 1% to 6% of the total conformational population or up to 10% with respect to the most populated conformer. This value is not negligible and opens good perspectives for the successful experimental identification of the C_s form.

Along with sufficient population of the minor conformer in the gaseous phase, another important prerequisite for its observation in matrices is the value of the energy barrier separating it from the lower energy minima. From Fig. 1, it is obvious that the conformational conversion of the two higher energy conformers of TMP into lower energy conformers involves, in each case, change of only one torsional coordinate. The C_s conformer can be transformed into the C_1 form by internal rotation of one of the lateral methyl groups from *gauche'* to *gauche* position, with the methyl group in the *trans* position retaining its orientation. The C_1 form can be transformed into C_3 by rotation of the *trans* methyl group towards the *gauche* orientation. These two internal rotations should then be investigated in detail. The next issue would be the choice of the theory level for evaluation of the relevant details of the potential energy surface of TMP. From Table 1, it can be seen that the relative conformational energies obtained with the 6-31G(d,p) basis set correspond fairly well to the values obtained with basis sets including diffuse functions (both for MP2 and DFT calculations). Since the monomer of TMP cannot form strong intramolecular hydrogen bonds, inclusion of diffuse functions should not play a crucial role in the calculations of the energy. Other parameters, like electronic spatial extent and molecular dipole moment (they will be discussed in this Letter later), are also reproduced well enough comparing to other levels of theory. Thus, the 6-31G(d,p) should be the basis set of choice, considering the necessary com-

promise between the cost of calculations and credibility of the results.

The scans of the potential energy surface were performed with the 6-31G(d,p) basis set using both the MP2 and DFT methods. The results of these scans are presented in Fig. 2. The potential energy profiles obtained at the two levels of theory are very similar, the DFT calculations slightly underestimating the values of barriers comparatively to the MP2 method. For the transformation of the C_s conformer into the C_1 form, the barrier height is 0.3 (DFT) or 0.9 (MP2) kJ mol^{-1} (Fig. 2, frame A). This value is sufficiently low and conformational cooling between this pair of conformers should readily occur in the matrix. For the transformation between the C_1 and the C_3 forms, the calculated barrier is much higher – 7.7 (DFT) or 9.8 (MP2)

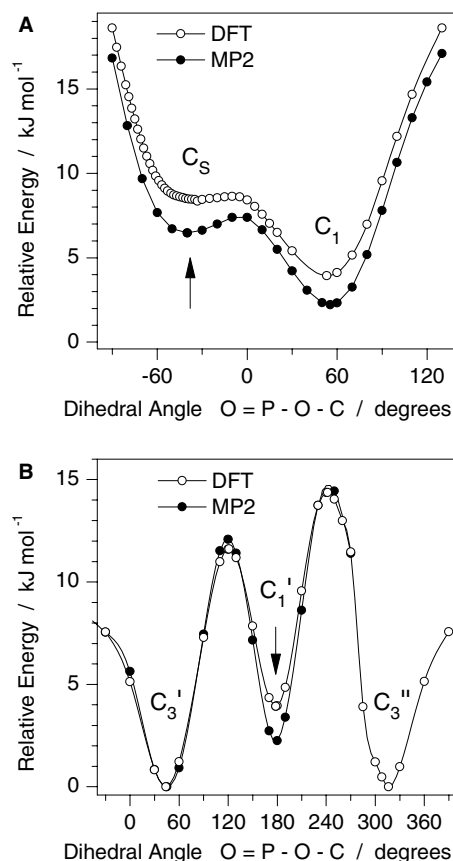


Fig. 2. Barriers to internal rotation in the molecule of trimethyl phosphate calculated at the DFT(B3LYP) and MP2 levels of theory with the 6-31G(d,p) basis set. Note that the driving coordinates (abscissas) in the two frames are different. The barrier separating the C_s and C_1 forms (A), corresponds to rotation of one methyl group from *gauche'* to *gauche* orientation. In the case of the barrier between the C_1 and C_3 forms (B), another methyl group changes its orientation from *trans* to *gauche* (or to *gauche'* if rotated in opposite direction). Vertical arrows indicate starting geometries for the scans, which within each pair of conformers correspond to the higher energy local minimum, C_s (A) and C_1 (B). In both frames the zero energy level corresponds to the energy of the C_3 form (zero point vibrational energy is not included).

kJ mol^{-1} (Fig. 2, frame B). Since the C_1 form is asymmetric, rotation from the *trans* methyl orientation was investigated in two possible directions. Scan in the opposite direction yielded even higher barrier values: 10.4 and 12.2 kJ mol^{-1} for DFT and MP2 methods, respectively. This result means that conformational cooling between the C_1 and C_3 forms should occur at much higher temperatures with respect to the pair C_s and C_1 . An additional note should be made, stressing that the calculations in Fig. 2 represent values of the barriers in the gaseous phase. In matrices, bulky methyl substituents may face matrix host atoms as a steric hindrance for internal rotation and the effective barriers in matrices could be higher than the calculated values. The fact that introduction of a methyl substituent may increase the effective height of the barriers in the matrix can be demonstrated by comparison of results previously obtained for cyanoacetic acid and methyl cyanoacetate. These two molecules differ only by replacement of the carboxylic hydrogen atom by a methyl group and, in the gaseous phase, were shown to have the same barrier to internal rotation in the direction of the observed conformational cooling, amounting to 3 kJ mol^{-1} . However, the conformational cooling for the methyl substituted species was observed at much higher temperatures [33]. This observation constitutes an additional justification for our expectations regarding the possibility of successful trapping the C_s conformer in a low temperature matrix.

To finalize this theoretical section, it should be noted that we kept in mind the work of Khetrpal et al. [25], who obtained the NMR spectra of partially oriented molecules of TMP, and explained them in terms of the co-existence of two forms with threefold symmetry axis. These two forms differed by the values of the dihedral $\text{O}=\text{P}-\text{O}-\text{C}$ angles (ca. 60° and 155°). To check this hypothesis, we performed a scan of the TMP potential energy surface, conserving the overall C_3 symmetry and changing simultaneously and equally the three $\text{O}=\text{P}-\text{O}-\text{C}$ dihedral angles. In the vicinity of 155° , the energy was calculated to be ca. 53 kJ mol^{-1} higher than that of the most stable form, and no local minimum was found at the DFT(B3LYP)/6-31G(d,p) level. The only minimum obtained in this scan corresponded to the *gauche* orientation (44°) of the methyl groups with respect to the $\text{P}=\text{O}$ bond. In order to explore all symmetrical cases, a potential energy scan was also performed with conservation of the C_s symmetry. In this second scan, one of the methyl groups was kept in the *trans* position with respect to the $\text{P}=\text{O}$ bond, while the other two methyl groups were scanned from the (*gauche*, *gauche'*) position, via (*cis*, *cis*) geometry, towards the (*gauche'*, *gauche*) configuration. Again, only one true minimum was found in this scan. Details of the C_s scan will be addressed later in this Letter.

3.2. Infrared spectra

The infrared spectra of the TMP monomer were studied in two different matrix host gases. Argon was used for reference purposes. The spectra of TMP in argon obtained in this Letter perfectly correspond to those reported before [20,24]. In our experiments, TMP isolated in argon matrix exhibited multiple site-splitting, in consonance with the previous reports, and band shapes were highly reproducible comparing to the data published earlier. In addition, no extra bands due to impurities or associates could be found. The same isolation conditions used for argon were then applied in the xenon experiments. Rare gas flux during sample preparation was about 10 mmol h^{-1} , and the gas was deposited from room temperature. Argon was not used further because xenon has better relaxant properties and it is more appropriate choice to achieve the objectives of the present Letter.

A few notes shall be here done with respect to the assignment of the experimental absorption bands. In this respect TMP is a difficult system. Besides the vibrations of the CH_3 fragments, the $\text{P}=\text{O}$ stretching mode is the only vibration which is highly localized in one bond. It is commonly accepted that the band due to the $\text{P}=\text{O}$ stretching vibration appears in the vicinity of 1300 cm^{-1} . The remaining vibrations include stretching of the $\text{P}-\text{O}$ and $\text{O}-\text{C}$ bonds and deformations of the $\text{O}=\text{P}-\text{O}$, $\text{P}-\text{O}-\text{C}$ and $\text{O}-\text{P}-\text{O}$ angles. These vibrations are highly mixed. As early as in 1961, Popov et al. [12] wrote: '*frequencies in the 1000–1050 and 730–800 cm^{-1} regions can only very provisionally be identified with $\text{O}-\text{C}$ and $\text{P}-\text{O}$ vibrations because, although the $\text{C}-\text{O}$ bond (1000–1050 cm^{-1}) and the $\text{P}-\text{O}$ bond (730–800 cm^{-1}) play the major part in these vibrations, the bonds and angles of the organic part of the molecule also vary appreciably. At the same time, the phosphoryl group in $(\text{CH}_3\text{O})_3\text{PO}$... takes practically no part in these vibrations*'. Gorenstein et al. [29] demonstrated the existence of a direct coupling between $\text{C}-\text{O}-\text{P}$, $\text{O}-\text{P}-\text{O}$ and torsional angles in TMP. It must, however, be stressed that the detailed vibrational assignment is not the primary goal of this Letter. Indeed, it has no implications on the studied subject and conclusions. The assignment of the observed spectral bands here presented shall then be considered only as a rough approximate description of the vibrational coordinates. The next difficulty in infrared spectroscopic studies of TMP is related with its conformational isomerism. As it was mentioned by Sablinskas et al. [19], '*most of the calculated wavenumbers of bands belonging to different conformers [except for some bands ...] coincide. These calculations support the observation that both in the Raman and IR spectra of crystalline TMP very few bands vanish compared to the corresponding spectra of the liquid*'. In the present Letter, we have carefully searched for the above-mentioned

bands-exceptions. A few spectral regions with such vibrations were found and studies of the experimental bands in these regions allowed for a deeper look at the effect of conformational cooling in TMP.

In pursuit of experimental proofs for conformational cooling we performed two different kinds of experiments. In the first approach, the matrix was deposited at the lowest possible substrate temperature, 10 K, and then subjected to annealing. In the second approach, annealing of the sample was carried out simultaneously with deposition. To do this, the temperature of the matrix substrate was fixed (at 20, 30, 40, 50 or 60 K) during deposition of the samples and kept unchanged during registration of the spectra. Both approaches gave qualitatively the same results, with the only difference that annealing of the samples during deposition is more efficient, and all observed changes appear at slightly lower temperatures as compared to the annealing after deposition. Both approaches will be demonstrated here.

3.3. 1340–1230 cm^{-1} spectral region

This spectral region represents the absorptions due to the P=O stretching vibration and is shown in Fig. 3. As it is seen from this figure, the spectrum in this region has multiplet structure. The lower frequency band in the multiplet is centered at 1282.7 cm^{-1} , in xenon matrix, and is a match of the 1286.7 cm^{-1} feature observed in nitrogen matrix, previously assigned to the P=O stretch in TMP molecules with C_3 conformation [31]. The higher

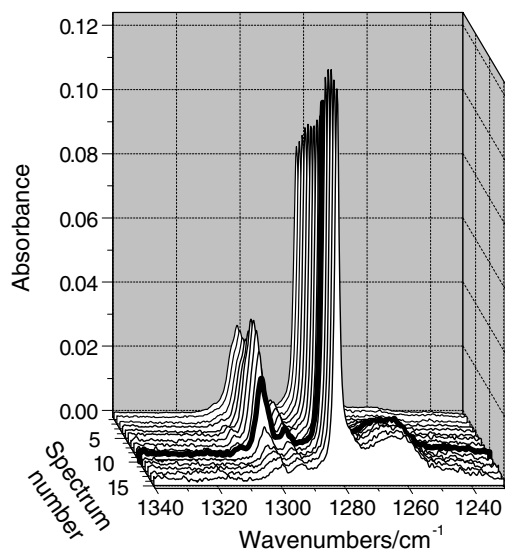


Fig. 3. The region of the P=O stretching vibration of trimethyl phosphate isolated in xenon matrix. Spectrum number 1 corresponds to the matrix deposited at 10 K. Spectra numbered from 2 to 10 were collected during matrix annealing, incrementing temperature of the optical substrate by steps of 5 K. Spectrum number 10 (temperature of the optical substrate equal to 55 K) is highlighted by the bold line. Spectra 11–15 were collected at 60, 60, 61, 62 and 62 K, respectively.

frequency band observed in xenon matrix is centered at 1301.5 cm^{-1} , with a shoulder at ca. 1295 cm^{-1} . In nitrogen matrix, the higher frequency feature was observed as a doublet at $1306.5/1301.7 \text{ cm}^{-1}$. Vidya et al. showed that this doublet was significantly depopulated when a supersonic jet source was used for deposition [22]. According to this behavior, and based on the subsequent theoretical calculations, the higher frequency doublet observed in nitrogen was assigned to the C_1 conformer [31]. From here onwards, for calculations carried out in this Letter, we will cite the non-scaled frequencies obtained at the DFT(B3LYP)/6-311++G(2d,2p) level of theory. Conformers C_3 and C_1 were predicted to have the bands due to the P=O stretching vibration at 1274 (193) and 1299 (241) cm^{-1} (in parentheses are given the calculated infrared band intensities in km mol^{-1}). Hence, these conformers are indeed good candidates for assignments. However, as discussed before, conformer C_s should not be neglected during analysis of the vibrational spectra of TMP, since this form is expected to be present in a significant amount in the gaseous phase immediately prior to deposition of the matrix. This conformer is predicted to have the P=O stretching vibration at 1298 (223) cm^{-1} , i.e., the predicted P=O stretching frequencies and intensities are practically equal for the C_1 and C_s forms (at this and all other theory levels). Thus, unequivocal assignment of the higher frequency feature to the C_1 conformer is not possible, since the C_s form can also contribute significantly to the observed band. The lower frequency component can be assigned to the C_3 form with a high confidence, since there are no bands due to other forms expected to appear at this frequency.

Now, with tentative assignments in mind, let us look at the experimental spectra with more detail (Fig. 3). On the first stage of annealing (in the temperature range 10–30 K), all spectral features became more sharp, with no loss of intensity. In the 30–45 K range both intensities and band profiles remain unchanged. However, at 50–55 K, the intensity of the band at 1290 – 1310 cm^{-1} decreases significantly (the spectrum corresponding to 55 K is shown by the bold line in Fig. 3). Concomitantly, the band centered at 1282 cm^{-1} continues to grow. At isothermal conditions (60–62 K) the higher frequency component practically disappears completely. The same results were obtained in the series of experiments where matrices were deposited with different temperatures of the optical substrate. In the 10–40 K interval the relative intensities within the doublet did not change; at 50 K, the higher frequency component was significantly depopulated; at 60 K it disappeared. The broad feature appearing between 1250 and 1270 cm^{-1} at higher temperatures can be unequivocally attributed to associated species.

The observed behavior matches previous findings [20,22], where no conformational cooling was observed

in the temperature range 10–35 K. More importantly, however, our results demonstrate that the conformational cooling of matrix-isolated TMP, for samples deposited with effusive source, is possible: it does occur in xenon matrices and is completed at ca. 60 K. Our observations and computations also support the assignment of the lower frequency component of the P=O stretching band to the C_3 conformer. However, as mentioned above, the assignment of the higher frequency component should be based on consideration of both C_1 and C_s forms. According to our theoretical expectations, conformational cooling between the C_s and C_1 forms should occur at temperatures lower than that between C_1 and C_3 . However, in the P=O stretching region the first process is impossible to be observed, since both C_1 and C_s forms absorb at the same frequency with the same intensity and no changes in the spectrum are then expected. The conformational cooling brings all conformers to the C_3 geometry. This form can be now considered as the lowest energy form in matrix. So, the matrix environment does not change the relative stability of the C_1 and C_3 conformers with respect to the gaseous phase and the C_3 form corresponds to the most stable conformer at both conditions.

3.4. 810–890 cm^{-1} region

The vibrations occurring in this region were described previously as P–O–(C) stretching [22], (P–O)–C vibration [20], asym. P–O–(C) stretching [10], ν_a PO_3 [17], ν_a (P–O) $_3$ [14], ν_a (P–O) $_3$ [9]. This diversity of descriptions reflects the complicated nature of the vibrations in question. We shall provisionally name the vibrations in the discussed region as POC ‘in-phase’ stretching, based on visualization of the molecular vibrations in the GAUSSVIEW program. During these vibrations, the P–O and O–C fragments linked to the same oxygen atom contract and expand in phase. Each conformer was predicted to have two vibrations in this region. The corresponding calculated frequency values are: 842 (124, two degenerated vibrations of E symmetry); 840 (141) and 823 (169); 832 (197, A') and 828 (92, A''), for the C_3 , C_1 and C_s forms, respectively. Fig. 4 represents these calculated data compared with the experiment. In this spectral range, both vibrations of the C_s conformer are predicted *not to coincide* with those due to other forms and can be experimentally distinguished if the C_s form is present in the sample.

The experimental spectra in Fig. 4 represent results of six depositions, with different temperatures of the optical substrate (specified in each frame) and other conditions equal. At the lowest substrate temperature (10 K) xenon solidifies very quickly and forms a disordered glass-like structure, rather than a crystal. At this condition the studied molecules are trapped in many different matrix cages and absorption bands are broadened due

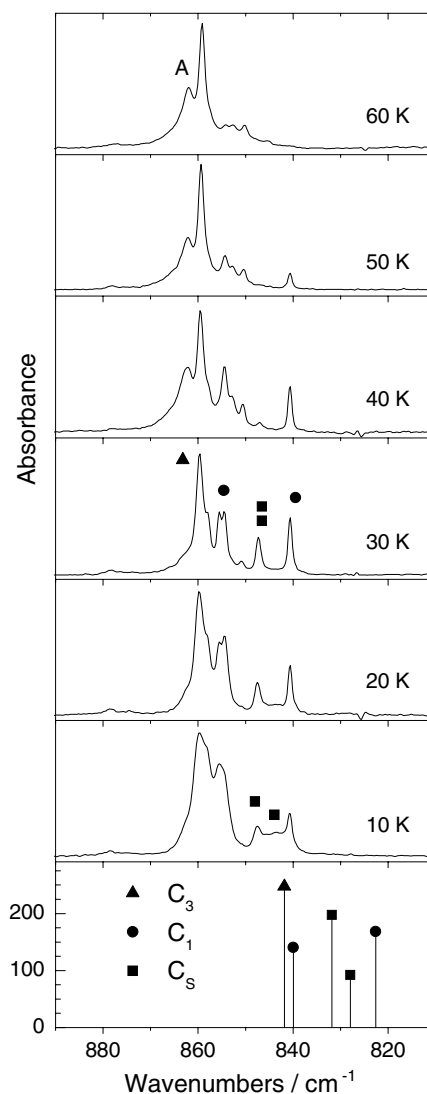


Fig. 4. Comparison of the experimental and the theoretical spectra of trimethyl phosphate (TMP) in the 890–810 cm^{-1} region. The six upper frames represent experimental spectra of TMP isolated in xenon matrices, deposited in independent experiments at different temperatures of the optical substrate. The lowest frame shows the spectra calculated at the DFT(B3LYP)/6-311++G(2d,2p) level of theory. Calculated frequencies are not scaled. Theoretical intensities (in km mol^{-1}) are given per one molecule (overall degeneracy is not taken into account). For the doubly-degenerated vibration of the C_3 conformer intensities are summed. The band designated by the letter ‘A’ is due to associates.

to the effect of the inhomogeneity of the environment. However, at this temperature conformational relaxation of the studied molecules in matrices is highly suppressed. It can be expected that at this temperature the distribution of conformers in matrix is maximally approached to the gaseous phase conditions prior to deposition. Comparison of the experimental spectrum with the theoretical predictions reveals two bands that can be assigned to the vibrations of the C_s form: a narrow band centered at 847.5 and a broader band centered at ca.

844 cm^{-1} (marked by squares in the frame '10 K'). The C_1 form can be assigned to the bands appearing at 854.5 and 840.7 cm^{-1} and the C_3 form to the band centered at ca. 859 cm^{-1} . The relative position of all observed bands corresponds very well to the theoretical predictions. This assignment can be confirmed by thermal behavior expected for each conformer. In the sample deposited at 20 K all conformers are still present in the matrix, but the respective bands are sharper, since an increase of the substrate temperature during deposition results in formation of a more relaxed matrix and the studied molecules have a smaller number of possible matrix cage environments. This trend continues to be observed in the sample deposited at 30 K. The band assignments to the different conformers are specified in the corresponding frame of Fig. 4 by triangle (C_3), circles (C_1) and squares (C_s). A surprising fact was the disappearance of one of the bands due to the C_s form at this temperature of deposition; we found an explanation for such observation and shall comment on it below.

The spectra of the samples obtained at 10–30 K were important for identification of the spectral signatures due to the individual conformers. The spectra of the samples deposited at higher temperatures will be important for characterization of the conformational cooling. In the sample deposited at 40 K, the absorptions due to the C_s form are absent, while those due to the C_1 and C_3 forms are still present. It can be concluded that the C_s form undergoes conformational cooling in the xenon matrix. It converts directly to the C_1 form, as confirmed by the annealing experiments in the 30–40 K temperature range. In argon, the corresponding temperature should be higher than in xenon [33], whereas nitrogen might be expected to behave similarly to argon in this respect. The consequence is that the samples of TMP deposited with effusive source in argon and nitrogen matrices should contain the C_s conformer too, not only C_3 and C_1 . Thus, the previous matrix studies of TMP in argon and nitrogen (e.g., [19,20,22]) might need to be revised taking into consideration the presence of the C_s form. In the sample deposited at 50 K, the bands due to the C_1 form are strongly depopulated, but still discernible. Thus, conformational cooling for the C_1 and C_3 pair occurs in the vicinity of 50 K. This temperature is slightly lower comparing to the annealing after deposition. This observation can be explained by the fact that on deposition the host atoms release excessive energy during crystallization and the effective temperature on the surface of growing matrix is higher than on the sample holder. This difference can amount to a few Kelvin, as deduced from the conformational cooling data. Finally, in the samples deposited at 60 K, the conformational cooling is over and TMP is present only in one conformation, C_3 , which corresponds to the lowest energy form of TMP in matrix media.

3.5. C_s scan

Let us return now to the peculiarities of the spectrum originated by the C_s form. After additional theoretical considerations we found an explanation for the spectrum observed at 30 K (Fig. 4), in particular, the disappearance of one of the bands compared to the depositions undertaken at lower temperatures. As it was mentioned in the theoretical section, we scanned the potential energy surface of the TMP monomer within the C_s symmetry framework. For the C_s scan, the two O=P–O–C dihedral angles were changed incrementally, in the mirror-like manner, so that the overall symmetry remained C_s . This scan revealed a very flat potential energy surface in the range of dihedral angles from -50° to $+50^\circ$ (Fig. 5, frame A). We suppose that due to a high flexibility along this coordinate, the TMP monomer can undergo geometrical distortion in matrix, which can result in spectral changes. Such effect has already been observed in matrix isolated molecules [35]. In order to verify this hypothesis, in addition to the potential energy scan, frequency calculations were performed at all partially optimized geometries. The frequencies obtained in the 820–850 cm^{-1} region are presented in frame B (Fig. 5).

At the minimum geometry (the O=P–O–C dihedral angles have a value of 33° and opposite signs), the two POC frequencies stay apart by ca. 3 cm^{-1} . The calculations predict that, when the two dihedral angles are in the range from 45° to 50° , the two POC frequencies converge within 0.5 cm^{-1} (towards the higher-frequency band). This is exactly what is observed in the experiment at 10–30 K: the band centered at 847.5 cm^{-1} intensifies, while the band at 844 cm^{-1} gradually vanishes (see Fig. 4). At the geometry where the two frequencies are the closest (dihedral angles are equal to 45°), the energy of molecule augments only by 0.9 kJ mol^{-1} with respect to the gaseous phase minimum. In matrices, destabilization due to geometrical distortions can be compensated due to various kinds of interactions between the studied guest molecule and the matrix gas host. As it was commented in the introduction, in the very case of the TMP molecule, the most polar C_1 form becomes highly stabilized in polar solvents. Similarly, a slight stabilization of the C_s geometry in matrices can occur if its dipole moment increases. During distortion of the dihedral angles from 33° to 45 – 50° , the molecular dipole moment of the C_s form (frame C) changes from 2.8 to 3.2/3.4 Debye. The electronic spatial extent (frame D), which is often used as a measure of the molecular volume, simultaneously decreases – the C_s form becomes more 'compact' and can be better packed in a matrix cavity. Thus we suggest that the interplay of energetic, polarization and spatial factors results in deformation of the C_s conformer in the matrix with respect to the equilibrium structure in the gaseous phase. This hypothesis is

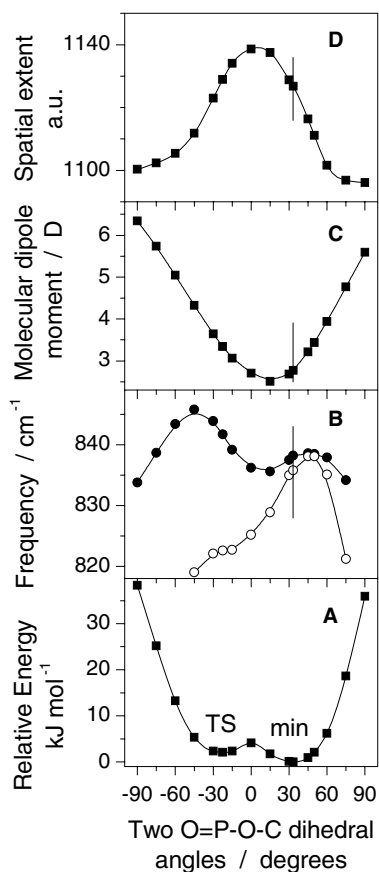


Fig. 5. Changes in relative energy (A), vibrational spectrum (B), dipole moment (C) and electronic spatial extent (D) of the trimethyl phosphate monomer during simultaneous rotation of the two methyl groups, with C_s symmetry imposed onto the molecule. Calculation at the DFT(B3LYP)/6-31G(d,p) level of theory. The dihedral angles for the scanned methyl groups have always the same value and opposite sign. Relative energies (A) are calculated with respect to the energy of the C_s form, without the zero point vibrational energy contribution. Point at 33.2° (min) corresponds to the true minimum (the C_s conformer) and point at -22.6° (TS) is a first-order saddle point. Black circles (B) refer to the A' mode (P–O–C ‘in-phase’ stretching vibration of the group lying in the symmetry plane; the corresponding methyl group has always *trans* orientation with respect to the P=O bond). White circles (B) correspond to the A'' mode (antisymmetric P–O–C ‘in-phase’ stretching vibration of the two remaining groups). Vibrational frequencies are not scaled. Vertical lines (B, C, D) are drawn at the abscissa corresponding to the minimum of energy.

confirmed by the change in the absorption spectra observed for the samples deposited at 10, 20 and 30 K (see Fig. 4). Moreover, in this temperature interval, diffusion of the guest molecules is strongly suppressed in xenon matrices. Thus, all structural changes observed for conformer C_s should take place in the monomer (and do not result from association). Note also that, reinforcing our interpretation, practically the same changes in the spectra are observed in the sample deposited at 10 K and subsequently annealed to 30 K.

A minor note should be made with respect to the shape of the calculated barrier (Fig. 5). It has two seeming minima, but calculation of the vibrational frequen-

cies for the geometry in the vicinity of -23° (designated as ‘TS’) yields one imaginary frequency (70 (i) cm^{-1}). This normal mode corresponds to the anti-symmetric change of the two O=P–O–C dihedral angles in the direction of the C_1 conformer. It should be noted that deformation of the C_s geometry in the matrix occurs in the direction away from the C_1 form. The dipole moment becomes almost equal in the ‘distorted C_s ’ and C_1 forms. These two factors, in combination, are likely to result in an increase of the barrier separating these two forms in matrices. That is why the conformational cooling from the C_s to the C_1 form occurs at higher temperatures than it could be expected on the base of the gas-phase calculated barrier (Fig. 2).

3.6. 1000–1100 cm^{-1} region

Having found evidence about the presence of the C_s conformer in the matrices by analysis of the 810–890 cm^{-1} spectral region, it would be interesting to find spectral manifestations of this form in other spectral regions. Indeed, despite as already mentioned almost all vibrations of the C_s form coincide in frequency with bands originated in other conformers, there is another spectral region where the vibrational signature of the C_s conformer can be clearly observed. The vibrations in this region can be provisionally designated as POC ‘anti-phase’ stretching and are the most intense in the spectrum of each conformer. Each conformer has two vibrations in the discussed region. The A'' symmetry vibration of the C_s conformer appears at the lowest frequency both in calculations [1040.3 cm^{-1} ($629.6 \text{ km mol}^{-1}$)] and in the experiment 1036.5 cm^{-1} (in xenon matrix). Increase of the sample temperature above 30 K results in decrease of intensity of this band (concomitantly with the above-mentioned band due to the C_s form at 847.5 cm^{-1}), while the neighboring bands originated by the other conformers continue to grow. The characteristic behavior of the 1036.5 cm^{-1} band during the annealing of the matrix (Supplementary Information, Fig. S1) as well as the good correspondence of the theoretical and calculated values allow to assign it to the C_s form with all certainty.

4. Conclusion

This Letter reports the conformational study of trimethyl phosphate monomer carried out by the joint usage of matrix-isolation, FTIR spectroscopy and theoretical approaches. Existence in both the gaseous phase and inert cryogenic matrices of the three predicted theoretically conformers, with C_3 , C_1 and C_s symmetries, has been unequivocally demonstrated experimentally for the first time. The energy barriers separating these conformers were calculated at the DFT and MP2 levels of theory

with the 6-31G(d,p) basis set and their vibrational spectra predicted using a large variety of basis sets of different sizes. At temperatures from 20 to 30 K, the C_s conformer undergoes a slight geometrical distortion, which gives rise to clearly observable changes in its vibrational signature. The reasons for this geometrical distortion were discussed and interpreted based on the theoretical calculations, being related with the stabilization, in the matrix, of a slightly more polar and compact geometry in the vicinity of the C_s minimum existing in the gaseous phase and initially deposited in the matrix. TMP was found to be a paradigmatic example of a system where sequential conformational cooling of a molecule isolated in a low temperature inert matrix occurs. Upon increasing the temperature above 30 K, conformational relaxation of the C_s towards the lower-energy C_1 form is observed. This observation is in compliance with a low barrier separating the C_s and C_1 forms in the gaseous phase. On the other hand, the barrier separating the C_1 form from the global energy minimum C_3 is much higher in the gaseous phase. Correspondingly, the conformational cooling of TMP towards the C_3 conformer takes place only at higher temperatures (in the 40–60 K range). For the first time it was shown (i) the presence of the C_s conformer in matrices, (ii) that the most stable form in matrices is the C_3 and (iii) that conformational cooling of TMP in matrices is possible.

Acknowledgment

The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT), Lisbon, for financial support (Grant SFRH/BPD/1661/2000).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at [doi:10.1016/j.cplett.2005.02.067](https://doi.org/10.1016/j.cplett.2005.02.067).

References

- [1] F. Weger, *Justus Liebig's Annalen der Chemie* 221 (1883) 61.
- [2] M.J. Cavalier, *Bulletin de la Société Chimique de Paris* 19 (1898) 883.
- [3] D.P. Evans, W.C. Davies, W.J. Jones, *Journal of the Chemical Society* (1930) 1310.
- [4] T.H. Connor, *Mutation Research* 65 (1979) 121.
- [5] S.S. Epstein, W. Bass, E. Arnold, Y. Bishop, *Science* 168 (1970) 584.
- [6] P.J. Hanna, J.B. Kerr, *Experientia* 37 (1981) 999.
- [7] O.A. Raevskii, A.N. Vereshchagin, F.G. Khalitov, *Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science* (1972) 305.
- [8] A.V. Yarkov, O.A. Raevskii, *Journal of General Chemistry of the USSR* 55 (1985) 42.
- [9] R. Streck, A.J. Barnes, W.A. Herrebout, B.J. van der Veken, *Journal of Molecular Structure* 376 (1996) 277.
- [10] F.S. Mortimer, *Spectrochimica Acta* 9 (1957) 270.
- [11] L.S. Mayants, E.M. Popov, M.I. Kabachnik, *Optika i Spektroskopiya* 7 (1959) 170.
- [12] E.M. Popov, M.I. Kabachnik, L.S. Mayants, *Russian Chemical Reviews* 30 (1961) 362.
- [13] O.A. Raevskii, A.N. Vereshchagin, Y.A. Donskaya, A.G. Abul'khanov, Y.A. Levin, *Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science* 25 (1976) 1889.
- [14] G. Mastrantonio, C.O. Della Vedova, *Journal of Molecular Structure* 561 (2001) 161.
- [15] G. Eaton, L. Harris, K. Patel, M.C.R. Symons, *Journal of the Chemical Society – Faraday Transactions* 88 (1992) 3527.
- [16] N. Tekin, M. Cebe, *Vibrational Spectroscopy* 36 (2004) 129.
- [17] K. Taga, N. Hirabayashi, T. Yoshida, H. Okabayashi, *Journal of Molecular Structure* 212 (1989) 157.
- [18] F. Marsault-Hérial, *Journal De Chimie Physique et de Physico-Chimie Biologique* 68 (1971) 274.
- [19] V. Sablinskas, A. Horn, P. Klæboe, *Journal of Molecular Structure* 349 (1995) 157.
- [20] L. George, K. Sankaran, K.S. Viswanathan, C.K. Mathews, *Applied Spectroscopy* 48 (1994) 7.
- [21] K. Sankaran, V. Vidya, K.S. Viswanathan, L. George, S. Singh, *Journal of Physical Chemistry A* 102 (1998) 2944.
- [22] V. Vidya, K. Sankaran, K.S. Viswanathan, *Chemical Physics Letters* 258 (1996) 113.
- [23] V. Vidya, K. Sankaran, K.S. Viswanathan, *Journal of Molecular Structure* 442 (1998) 251.
- [24] K. Sundararajan, V. Vidya, K. Sankaran, K.S. Viswanathan, *Spectrochimica Acta Part A – Molecular and Biomolecular Spectroscopy* 56 (2000) 1855.
- [25] C.L. Khetrapal, G. Govil, H.J.C. Yeh, *Journal of Molecular Structure* 116 (1984) 303.
- [26] H. Oberhammer, *Zeitschrift für Naturforschung – Teil A. Physik, Physikalische Chemie, Kosmophysik* 28a (1973) 1140.
- [27] M.J. Aroney, L.H.L. Chia, R.J.W. Le Fèvre, J.D. Saxby, *Journal of the Chemical Society* (1964) 2948.
- [28] U. Becker, V. Wessels, G. Turkey, A. Ghoneim, M. Stockhausen, *Zeitschrift für Physikalische Chemie – International Journal of Research in Physical Chemistry and Chemical Physics* 191 (1995) 251.
- [29] D.G. Gorenstein, D. Kar, B.A. Luxon, R.K. Momii, *Journal of the American Chemical Society* 98 (1976) 1668.
- [30] J.R. Van Wazer, C.S. Ewig, *Journal of the American Chemical Society* 108 (1986) 4354.
- [31] L. George, K.S. Viswanathan, S. Singh, *Journal of Physical Chemistry A* 101 (1997) 2459.
- [32] M. Baudler, *Zeitschrift für Elektrochemie* 59 (1955) 173.
- [33] I.D. Reva, S.G. Stepanian, L. Adamowicz, R. Fausto, *Chemical Physics Letters* 374 (2003) 631.
- [34] M.J. Frisch et al., *GAUSSIAN 98*, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.
- [35] I.D. Reva, S.G. Stepanian, L. Adamowicz, R. Fausto, *Journal of Physical Chemistry A* 107 (2003) 6351.