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# Molecular structure and infrared spectra of 3,4-dihydroxy-3-cyclobutene-1,2-dione; experimental matrix isolation and theoretical Hartree–Fock and post Hartree–Fock study

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## Abstract

The infrared spectra of 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) isolated in low-temperature Ar and $N_2$ matrices are reported. The comparison of the experimental spectra with those theoretically calculated at HF/6-31++G**, MP2/6-31G** and DFT(B3-LYP)/6-31++G** levels shows that the molecules of the compound isolated in low-temperature matrix adopt the structure with $C_{2v}$ symmetry. This structure is different from the one which was found in the crystal. Theoretical calculations of relative energies of $C_{2v}$ and $C_s$ structures predict the $C_{2v}$ conformation to be lower in energy by 8 kJ mol$^{-1}$. Good agreement between the experimental and theoretical spectra allowed for a reliable assignment of the observed IR absorption bands. © 1997 Elsevier Science B.V.

*Keywords:* Squaric acid; IR spectra; Matrix isolation

## 1. Introduction

Last years various derivatives of cyclobutenedione attracted the interest of scientists and practitioners. Because of their many unusual properties they can be exploited in different fields, starting from pharmacology, as antiulcer agents [1,2], analgestics for the treatment of pain and prostaglandin E antagonists [3], smooth muscle relaxants [4], as fluorescent dye compounds used to determine nucleic acids, number of microbial cells, cancer cells and gene copies [5], as photosensitizers in photographic materials [6] and polymerization processes [7], or even as an anode material for the new generation of solid-state batteries [8].

The title compound, 3,4-dihydroxy-3-cyclobutene-1,2-dione, also known under the name of squaric acid, is one of the smallest and simplest derivatives of cyclobutenedione. It is a chemically stable, highly acidic, colorless crystalline substance with the melting point above 300°C. Its

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crystal structure consists of the layers of nearly flat molecules, where each molecule is bonded to four neighboring units by four strong OH···O hydrogen bonds (2.54 Å), the layers being bonded together by mainly dipolar van der Waals interactions [9]. It is well established that at the temperature of 374 K crystal of squaric acid undergoes a structural transition [10,11]. Below this critical temperature each molecule has well defined single and double bond structure with two vicinal and two distal protons in an ordered arrangement. In the high-temperature regime the protons are equally distributed on two equivalent principal sites in the O···H···O hydrogen bonds.

In this work we report the IR spectra of monomeric squaric acid, trapped in low-temperature Ar and $N_2$ matrices together with the vibrational spectra calculated using HF, MP2 and DFT(B3-LYP) methods. The relative energies of $C_{2v}$ and $C_s$ conformers of the compound are also accounted for.

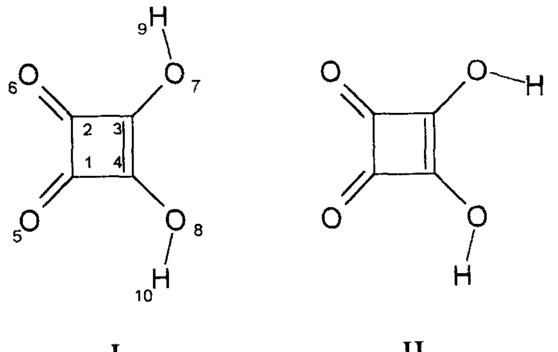
## 2. Experimental

The method of matrix preparation was similar to that described elsewhere [12]. The sample of squaric acid (Aldrich) was placed in the microoven in the vacuum chamber of the continuous-flow helium cryostat. The vapors of the compound coming out from the heated microoven were mixed with matrix gas (precooled in a liquid nitrogen trap) and deposited on a CsI window mounted on the cold finger (10 K) of the cryostat. The matrix gases, argon (Linde AG) and nitrogen (Technische Gase, Leipzig), were of purity grade 6.0. The infrared spectra were recorded with Perkin–Elmer 580B spectrometer operating at the resolution 1–3 cm$^{-1}$. Integral intensities of the absorption bands were measured by numerical integration.

## 3. Computational

The optimizations of the geometry of the squaric acid molecule were performed at HF/6-31 + + G**, MP2/6-31G** and DFT(B3-LYP)/6-31 + + G** levels using the gradient procedures of the GAUSSIAN 94 DFT program [13]. The diffused orbitals designated by '+ +' in the basis set specification were added to the basis set in the HF and DFT calculations to better describe the partial intramolecular hydrogen bonds, which can be formed due to the interaction of the hydrogens in the hydroxyl groups with the carbonyl oxygens. Next, the harmonic vibrational frequencies and the IR intensities were calculated at the same levels of theory. In order to approximately correct for the neglected part of electronic correlation, the basis set truncation and the vibrational anharmonicity effects, the calculated wavenumbers of all normal modes were uniformly scaled down by a single factor of 0.98 (DFT(B3-LYP)), 0.96 (MP2) and 0.9 (HF). The theoretically calculated force constant matrices in the Cartesian coordinates were transformed to the molecule fixed internal coordinates in order to enable the standard PED analysis [14] of the normal modes. The atom numbering is shown in Scheme 1 and the internal coordinate set used in the PED calculation is given in Table 1.

Squaric acid is a molecule with strained four-membered ring. For such a molecule one may expect a somewhat larger contribution from the non-dynamic electron correlation effects than in molecules in which the bond angles correspond to the particular hybridization pattern of the valence orbitals of involved atoms. It is therefore necessary to account for these correlation effects in both the structure optimization and in the calcula-



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Scheme 1.

Table 1
Internal coordinates used in the normal mode analysis for 3,4-dihydroxy-3-cyclobutene-1,2-dione (atom numbering as in Scheme 1)

| | |
|---|---|
| $A_1$ | |
| $S_1 = 2^{-1/2}\ (r_{7,9} + r_{8,10})$ | $\nu_s$OH |
| $S_2 = 2^{-1/2}\ (r_{3,7} + r_{4,8})$ | $\nu_s$C–O |
| $S_3 = 2^{-1/2}\ (r_{2,6} + r_{1,5})$ | $\nu_s$C=O |
| $S_4 = 2^{-1/2}\ (r_{2,3} + r_{1,4})$ | $\nu_s$C–C |
| $S_5 = r_{1,2}$ | $\nu C_1 - C_2$ |
| $S_6 = r_{3,4}$ | $\nu C_3 = C_4$ |
| $S_7 = 2^{-1/2}\ (\beta_{3,9,7} + \beta_{4,10,8})$ | $\beta_s$OH |
| $S_8 = \frac{1}{2}\ (\beta_{1,6,2} - \beta_{3,6,2} + \beta_{2,5,1} - \beta_{4,5,1})$ | $\beta_s$C=O |
| $S_9 = \frac{1}{2}\ (\beta_{4,7,3} - \beta_{2,7,3} + \beta_{3,8,4} - \beta_{1,8,4})$ . | $\beta_s$C–O |
| $B_2$ | |
| $S_{10} = 2^{-1/2}\ (r_{7,9} - r_{8,10})$ | $\nu_a$OH |
| $S_{11} = 2^{-1/2}\ (r_{3,7} - r_{4,8})$ | $\nu_a$C–O |
| $S_{12} = 2^{-1/2}\ (r_{2,6} - r_{1,5})$ | $\nu_a$C=O |
| $S_{13} = 2^{-1/2}\ (r_{2,3} - r_{1,4})$ | $\nu_a$C–C |
| $S_{14} = 2^{-1/2}\ (\beta_{3,9,7} - \beta_{4,10,8})$ | $\beta_a$OH |
| $S_{15} = \frac{1}{2}\ (\beta_{1,6,2} - \beta_{3,6,2} - \beta_{2,5,1} + \beta_{4,5,1})$ | $\beta_a$C=O |
| $S_{16} = \frac{1}{2}\ (\beta_{4,7,3} - \beta_{2,7,3} - \beta_{3,8,4} + \beta_{1,8,4})$ | $\beta_a$C–O |
| $S_{17} = \frac{1}{2}\ (\beta_{3,1,4} - \beta_{4,2,1} + \beta_{1,3,2} - \beta_{2,4,3})$ | $\beta$R |
| $B_1$ | |
| $S_{18} = 2^{-1/2}\ (\gamma_{6,1,2,3} - \gamma_{5,2,1,4})$ | $\gamma_s$C=O |
| $S_{19} = 2^{-1/2}\ (\gamma_{7,2,3,4} - \gamma_{8,1,4,3})$ | $\gamma_s$C–O |
| $S_{20} = \frac{1}{2}\ (\tau_{9,7,3,4} + \tau_{9,7,3,2} - \tau_{10,8,4,3} - \tau_{10,8,4,1})$ | $\tau_s$OH |
| $A_2$ | |
| $S_{21} = 2^{-1/2}\ (\gamma_{6,1,2,3} + \gamma_{5,2,1,4})$ | $\gamma_a$C=O |
| $S_{22} = 2^{-1/2}\ (\gamma_{7,2,3,4} + \gamma_{8,1,4,3})$ | $\gamma_a$C–O |
| $S_{23} = \frac{1}{2}\ (\tau_{9,7,3,4} + \tau_{9,7,3,2} + \tau_{10,8,4,3} + \tau_{10,8,4,1})$ | $\tau_a$OH |
| $S_{24} = \frac{1}{2}\ (\tau_{4,1,2,3} - \tau_{1,2,3,4} + \tau_{2,3,4,1} - \tau_{3,4,1,2})$ | $\tau$R |

Where $r_{i,j}$ is the distance between atoms $A_i$ and $A_j$; $\beta_{i,j,k}$ is the angle between vectors $A_kA_i$ and $A_kA_j$; $\gamma_{i,j,k,l}$ is the angle between the vector $A_kA_i$ and the plane defined by atoms $A_j$, $A_k$, $A_l$; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by $A_i$, $A_j$, $A_k$ and the plane defined by $A_j$, $A_k$, $A_l$ atoms.

tion of the vibrational frequencies. As it will be shown later, consistently with the above remark, the MP2 and DFT results are closer to the experimental data than the HF results.

## 4. Results and discussion

### 4.1. Structure of isolated molecule

The two most stable conformations of squaric acid may be considered as possible structures of the molecule isolated in the matrix. These structures are shown in Scheme 1: one of $C_{2v}$ symmetry (**I**) and the second of $C_s$ symmetry (**II**). The geometries of $C_{2v}$ and $C_s$ conformers of the squaric acid optimized at MP2/6-311 + + G** level are given in Table 2. The theoretical calculations of internal energies indicated that the conformer **I** ($C_{2v}$ symmetry) is most stable. The values of electronic energies obtained at MP2(full)/6-311 + + G**//HF/6-31 + + G** level are: $E_{el}(\mathbf{I}) = -453.6206649$ a.u. and $E_{el}(\mathbf{II}) = -453.6174464$ a.u. The difference of internal energies is $\Delta E = E_{el}(\mathbf{I}) - E_{el}(\mathbf{II}) + \Delta ZPE = -7.97$ kJ mol$^{-1}$ (the difference of zero point vibrational energies, $\Delta ZPE = ZPE(\mathbf{I}) - ZPE(\mathbf{II}) = 0.48$ kJ mol$^{-1}$, was obtained at MP2/6-31G** level).

The spectroscopic differentiation between two considered conformers is not straightforward. The theoretically predicted IR spectra of forms **I** and **II** are compared with experimental spectra in Figs. 1 and 2. According to the calculations, in high frequency region (near 3500 cm$^{-1}$) in the spec-

Table 2
Bond distances and bond angles at the geometry optimized at MP2/6-311 + + G** level

| | Form **I** | Form **II** |
|---|---|---|
| Bond distances (Å) | | |
| C1–C2 | 1.5521 | 15597 |
| C2–C3 | 1.4878 | 1.4945 |
| C3–C4 | 1.3818 | 1.3809 |
| C4–C1 | 1.4878 | 1.4851 |
| C1–O5 | 1.2093 | 1.2087 |
| C2–O6 | 1.2093 | 1.2041 |
| C3–O7 | 1.3229 | 1.3247 |
| C4–O8 | 1.3229 | 1.3303 |
| O7–H9 | 0.9674 | 0.9661 |
| O8–H10 | 0.9674 | 0.9668 |
| Bond angles[a] (°) | | |
| C4–C2–C3 | 93.280 | 93.220 |
| C3–C1–C4 | 93.280 | 93.662 |
| C4–C2–C1 | 86.720 | 86.706 |
| C1–C3–C2 | 86.720 | 86.412 |
| C2–O7–C3 | 133.136 | 130.250 |
| C1–O8–C4 | 133.136 | 134.514 |
| C3–O6–C2 | 133.925 | 136.011 |
| C4–O5–C1 | 133.925 | 134.191 |
| C3–H9–O7 | 107.826 | 109.489 |
| C4–H10–O8 | 107.826 | 108.220 |

[a] A–B–C is the angle between bonds A–C and B–C.

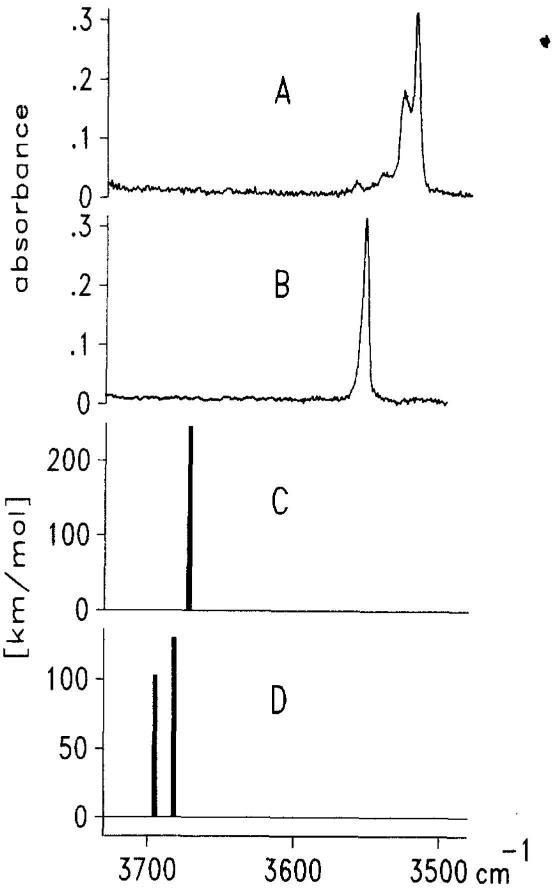

Fig. 1. The high frequency region of the IR spectrum of squaric acid. (A) experimental spectrum in $N_2$ matrix, (B) experimental spectrum in Ar matrix, (C) calculated at DFT (B-3LYP) level for conformer **I** of $C_{2v}$ symmetry, (D) calculated at DFT(B3-LYP) level for conformer **II** of $C_s$ symmetry.

trum of the conformer **I** the single absorption band due to $\nu$OH should be observed, while the absorption of the conformer **II** would be characterized by two bands with positions separated by 8 cm$^{-1}$. In the range 1900–200 cm$^{-1}$ (see Fig. 2), the theoretical predictions of the spectra of both forms do not differ more than the accuracy with which the calculations at the applied levels of theory usually reproduce the IR spectra [15]. For comparison with experimental results the theoretical spectra obtained at DFT(B3-LYP) level were used because, as it will be shown in the next section, this data fit best the experimental spectra. From this comparison one may conclude that only the pattern of the spectrum in the range of OH stretching vibration provides spectroscopic information on the conformation of isolated molecules. As it is seen in Fig. 1B, in the spectrum of squaric acid isolated in Ar matrix only one absorption band was observed. This indicates that molecules in the matrix adopt the structure of conformer **I** and supports the conclusion drawn from theoretical calculations of internal energy.

In the spectrum of the squaric acid in nitrogen matrix (Fig. 1A) the $\nu$OH band is split. We believe that this splitting is due to interactions of squaric acid molecules with $N_2$ environment and not due to the appearance of the conformer **II** in the matrix. The pattern of the splitting of $\nu$OH band differs from one $N_2$ matrix to the other. This may be seen by comparing the shape of the $\nu$OH band shown in Fig. 1A and Fig. 4A. Observed differences indicate that the splitting depends on the properties of matrix rather than on the spectral properties of the isolated molecules. In lower frequency range of the spectrum of squaric acid isolated in solid $N_2$ we observe weak bands which may testify to the existence of interactions with matrix. These bands are shown in Fig. 3. The bands marked with asterisks in trace C ($N_2$ matrix) correspond well to the bands which appear in Ar matrix after annealing of the matrix at 30 K—the bands marked with asterisks in trace B. The annealing of Ar matrix causes creation of associates which is clearly proven (Fig. 3B) by the appearance of a new band in $\nu_s$OH range at 3526, 3522 cm$^{-1}$.

The conformers of squaric acid in matrix (form **I**) are different from those in crystalline state (form **II**). It is possible that the hydrogen bonds in crystal stabilize the structure **II** more than the structure **I**.

### 4.2. *Infrared spectra*

Infrared spectra of squaric acid isolated in Ar and $N_2$ matrices, along with the results of theoretical simulations of the vibrational spectrum of the compound are presented in Fig. 4 and in Table 3.

As it was discussed earlier, the group of symmetry of squaric acid molecule in matrix is $C_{2v}$. It

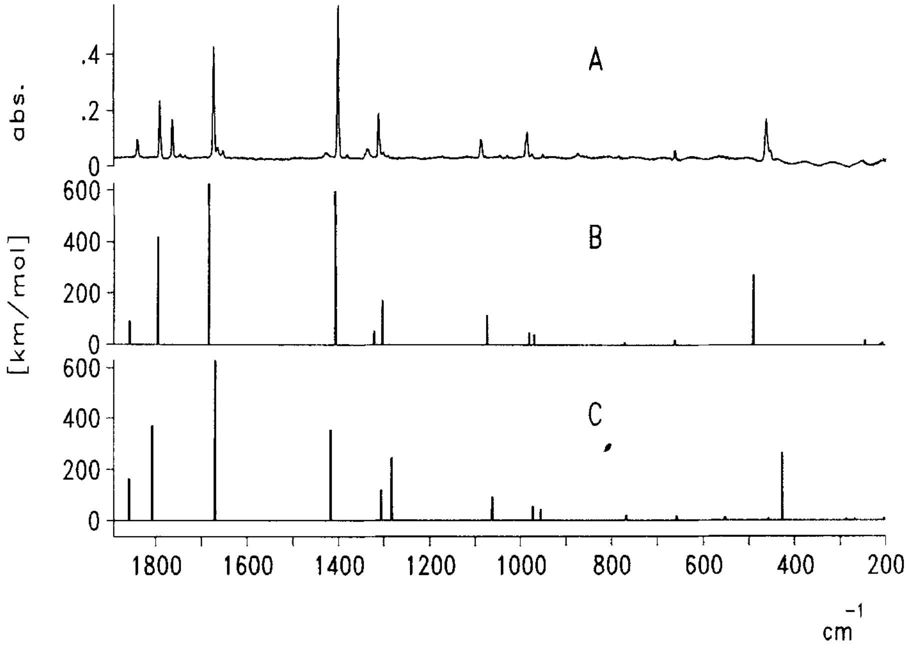

Fig. 2. The IR spectrum of squaric acid. (A) Experimental spectrum in Ar matrix, (B) calculated at DFT(B3-LYP) level for conformer **I** of $C_{2v}$ symmetry, (C) calculated at DFT(B3-LYP) level for conformer **II** of $C_s$ symmetry.

means that each vibration belongs to one of the four representations ($A_1$, $A_2$, $B_1$ and $B_2$). The vibrations belonging to $A_2$ representation are infrared inactive.

The band corresponding to the stretching vibration of OH groups was registered at 3552 cm$^{-1}$ in Ar matrix spectrum, and as a split band at 3525 and 3518 cm$^{-1}$ in $N_2$ matrix. In this spectral region all applied theoretical approaches predicted two modes due to conjugated stretching vibrations of the OH groups, namely very weak band due to symmetric stretching of both OH groups at 3674 cm$^{-1}$ (DFT), 3660 cm$^{-1}$ (MP2) and 3716 cm$^{-1}$ (HF), and strong band due to antisymmetric stretching of these groups at 3672 cm$^{-1}$ (DFT), 3659 cm$^{-1}$ (MP2) and 3714 cm$^{-1}$ (HF). The observed strong band is due to the $\nu_a$OH vibration; $\nu_s$OH does not manifest itself in the experimental spectra. In spite of applied scaling factors, theoretical calculations still overestimate the frequency of the band due to $\nu_a$OH by 120 cm$^{-1}$ (DFT), 107 cm$^{-1}$ (MP2) and 162 cm$^{-1}$ (HF), with respect to the Ar matrix spectrum. The $\nu$OH vibrations are more anharmonic than lower frequency vibrations. Therefore scaling of the wavenumbers with an uniform factor, bringing the predicted lower frequencies to values close to experimental, usually leads to overestimated frequencies of OH stretching vibrations.

The position of the $\nu$OH band in the spectrum of squaric acid is typical for the spectra of isolated molecules with OH groups involved in weak intramolecular interactions. For example, the bands due to analogous $\nu$OH vibrations of 2-hydroxypyridine [16] and 4-hydroxypyrimidine [17] were found at 3576 and 3564 cm$^{-1}$ (Ar), respectively.

In the region 1900–1750 cm$^{-1}$ the theoretical calculations predict two stretching vibrations of conjugated carbonyl groups. The high frequencies of the bands due to the carbonyl group are characteristic for the spectra of compounds in which the C=O group is attached to four (or three) membered ring with strained bonds and angles. From all three sets of calculations it appears, that the band due to the normal mode with dominant symmetric stretching vibration of C=O groups is weaker and positioned higher in frequency than that with the main contribution of antisymmetric stretching vibration of C=O groups. In this range of experimental spectrum we observe, however, three distinct absorptions instead of two theoretically predicted bands (see Fig. 4). The origin of this discrepancy between experimental results and theory is not clear.

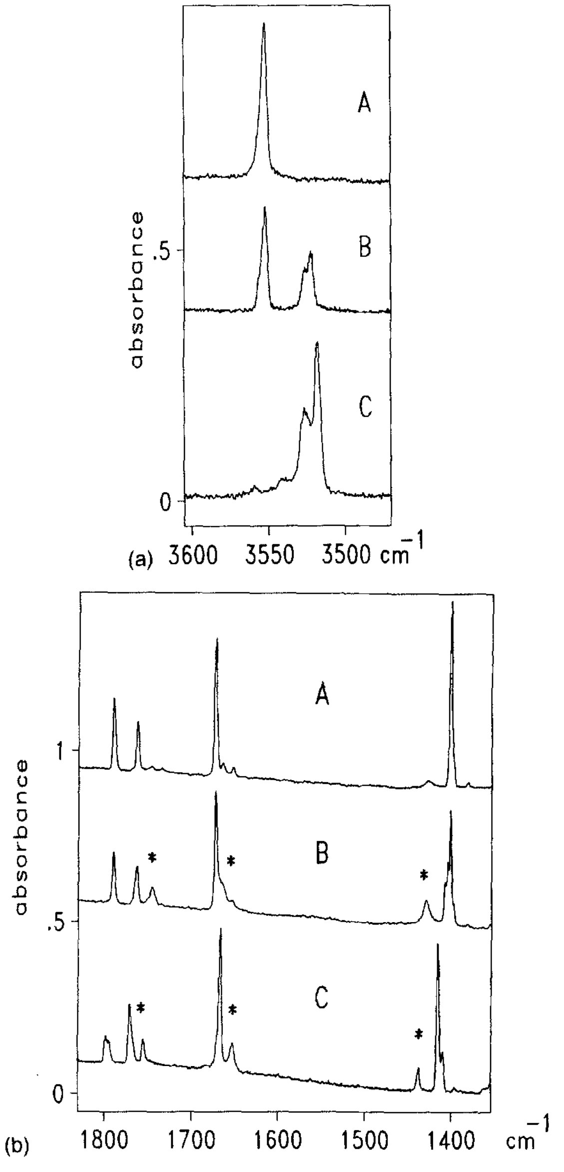

Fig. 3. Effect of association on the spectrum of squaric acid. (A) diluted Ar matrix, (B) Ar matrix after annealing at 30 K, (C) diluted $N_2$ matrix. The bands marked with asterisks—see text.

The highest-frequency experimental band in this spectral range, observed at 1838 cm$^{-1}$ in Ar and at 1839 cm$^{-1}$ in $N_2$ matrices, originates mainly from the symmetric carbonyl stretching. Unlike the HF calculations, both methods taking into account correlation effects predict that in the normal mode with frequency 1855 cm$^{-1}$ (DFT, for MP2, 1815 cm$^{-1}$) the $\nu_s$C=O is conjugated with stretching vibration of double $C_3$=$C_4$ bond and symmetric C–O vibration. All three theoretical approaches show that $\nu_s$C=O vibration, together with $\nu C_3$=$C_4$ and $\nu_s$C–O vibrations, is also involved in the normal mode, attributed to the strong band observed at 1673 cm$^{-1}$ (Ar) and at 1666 cm$^{-1}$ ($N_2$). The mode with major contribution from antisymmetric stretching vibration of two C–O single bonds manifests itself in the experimental spectra as a strong band at 1401 cm$^{-1}$ (Ar), (1415 cm$^{-1}$ (N2)).

The bands due to the normal modes with $\beta$OH vibrations involved dominate in the spectral region 1400–1000 cm$^{-1}$. The band due to antisymmetric, $\beta$OH vibration was observed at 1336 cm$^{-1}$ (Ar), 1353 cm$^{-1}$ ($N_2$), whereas symmetric, $\beta$OH vibration contribute to the bands at 1312 cm$^{-1}$ and 1087 cm$^{-1}$ (Ar), (1329 cm$^{-1}$ and 1089 cm$^{-1}$ ($N_2$)).

The bands occurring between 1000 and 950 cm$^{-1}$ in both matrices originate from the stretching C–C and C–O vibrations and deformational vibrations of carbonyl groups.

The spectral position of the band due to antisymmetric $\beta$C=O vibrations and antisymmetric $\beta$C–O vibrations (785 cm$^{-1}$, Ar) was well predicted at all applied levels of theory. The same is true for the band due to $\nu_s$C–C, $\nu_s$C–O and $\nu C_1$–$C_2$ vibrations, which was observed at 661 cm$^{-1}$ (Ar).

In the low frequency part of the spectrum the most characteristic, well-pronounced band is positioned at 463 cm$^{-1}$ (Ar). It can be attributed to symmetric torsional motions of OH groups. Analogous $\tau$OH bands were observed in the infrared Ar matrix spectra of 2-hydroxypyridine [16] at 467 cm$^{-1}$ and in the spectra of 4-hydroxypyrimidine [17] at 497 cm$^{-1}$. Theoretical predic-

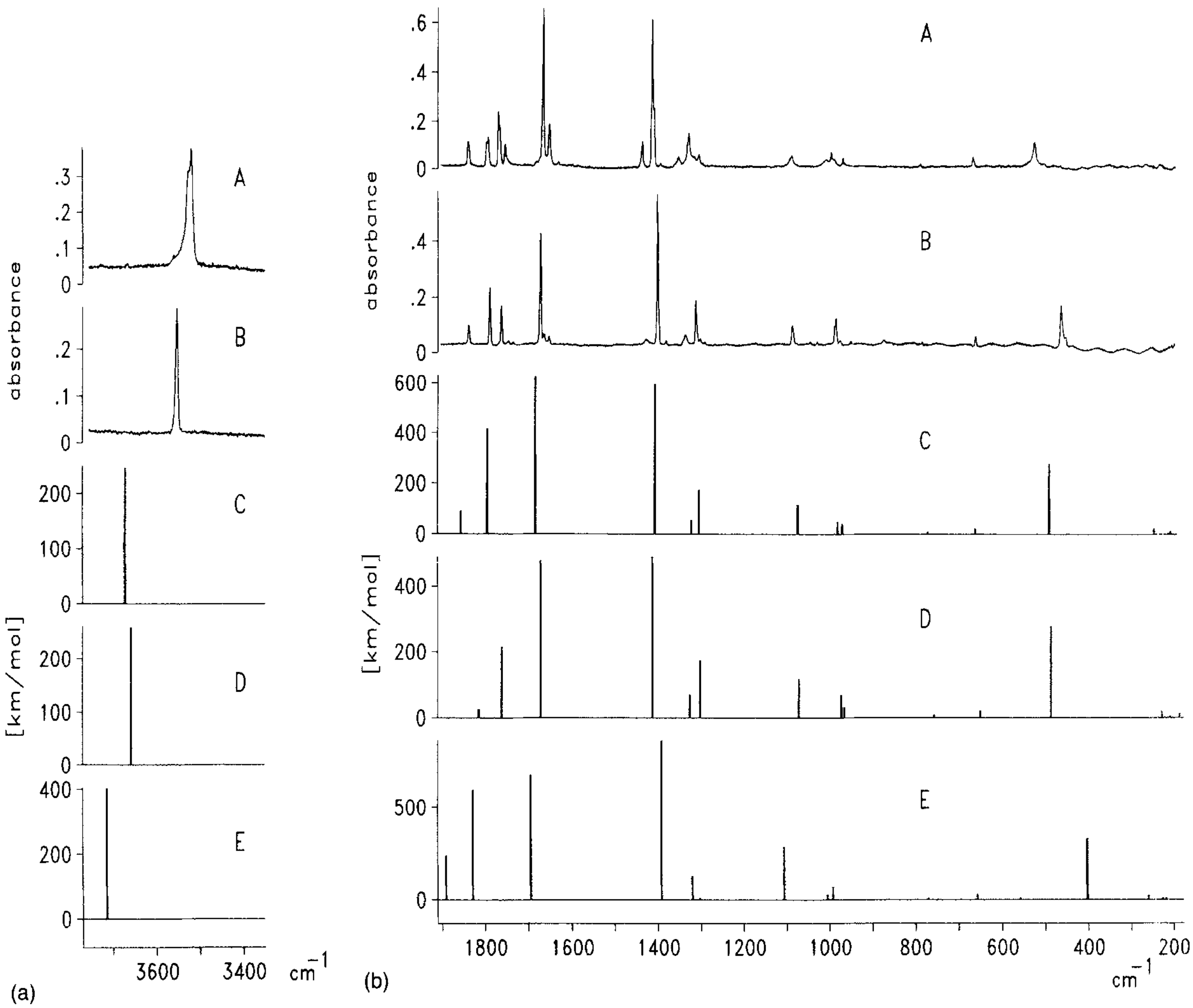

Fig. 4. Comparison between experimental and predicted theoretically spectra of squaric acid. (A) $N_2$ matrix, 10 K, (B) Ar matrix, 10 K, (C) calculated at DFT(B3-LYP)/6-31 + +G** level, (D) calculated at MP2/6-31G** level, (E) calculated at HF/6-31 + +G** level.

tion at HF level for squaric acid gave 402 $cm^{-1}$ as a position of the normal mode with a contribution from $\tau_s$OH vibration—about 60 $cm^{-1}$ lower than the position of this band in Ar matrix spectrum. As for both remaining theoretical approaches, they overestimate the $\tau_s$OH frequency by about 20–30 $cm^{-1}$ (namely: DFT by 27 $cm^{-1}$ and MP2 by 23 $cm^{-1}$) with respect to that observed for the equivalent band in Ar matrix spectrum. In $N_2$ matrix, the band due to torsion OH mode demonstrates typical high sensibility to the environmental changes and shifts towards higher frequencies, up to 527 $cm^{-1}$. The band due to $\tau_a$OH vibration with the predicted frequency 460 $cm^{-1}$ (DFT) is of zero intensity due to the symmetry reasons and was not observed in the experimental spectrum.

The detailed comparison of the three different theoretical methods of spectra simulation allows us to state that DFT and MP2 calculations, both taking into account correlation corrections, result with more reliable prediction of the frequencies of experimentally observed bands in the squaric acid spectrum than the calculations at the HF level.

Table 3

The experimental wavenumbers ($\tilde{\nu}$) and integral intensities ($I$) of the bands observed in the Ar and $N_2$ matrix spectra of squaric acid, compared with theoretically calculated wavenumbers, absolute intensities ($A$) and potential energy distribution (PEDs) of the absorption bands of $C_{2v}$ conformer of the compound

| Experimental | | | | Theoretical | | | | | | | PEDs | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ar matrix | | $N_2$ matrix | | Symmetry | DFT(B3-LYP)[a] | | M2[b] | | HF[c] | | Vibration | DFT (%) | MP2 (%) | HF (%) |
| $\tilde{\nu}$ (cm$^{-1}$) | $I$ (a.u.) | $\tilde{\nu}$ (cm$^{-1}$) | $I$ (a.u.) | | $\tilde{\nu}$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\tilde{\nu}$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\tilde{\nu}$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | | | | |
| | | | | $A_1$ | 3674 | 0.26 | 3660 | 0.7 | 3716 | 0.4 | $\nu_s$OH | 100 | 100 | 100 |
| | | 3525 sh | | | | | | | | | | | | |
| 3552 | 463 | 3518 | 759 | $B_2$ | 3672 | 247 | 3659 | 259 | 3714 | 404 | $\nu_a$OH | 100 | 100 | 100 |
| | | | | | | | | | | | $\nu_s$C=O | 63 | 57 | 71 |
| 1838 | 76 | 1839 | 61 | $A_1$ | 1855 | 93 | 1815 | 26 | 1890 | 238 | $\nu C_3=C_4$ | 13 | 14 | |
| | | | | | | | | | | | $\nu_s$C–O | 12 | 15 | |
| | | 1797 sh | | | | | | | | | | | | |
| 1789 | 204 | 1793 | 103 | $B_2$ | 1794 | 418 | 1761 | 261 | 1828 | 594 | $\nu_a$C=O | 87 | 86 | 88 |
| 1762 | 143 | 1770 | 158 | | | | | | | | | | | |
| 1746[d] | 7.4 | 1754 | 59 | | | | | | | | | | | |
| 1734 | 4.9 | | | | | | | | | | | | | |
| | | 1682 sh | | | | | | | | | | | | |
| 1673 | 498 | 1666 | 498 | $A_1$ | 1683 | 628 | 1671 | 479 | 1694 | 673 | $\nu C_3=C_4$ | 39 | 36 | 46 |
| 1664 | | 1652 | | | | | | | | | $\nu_s$C=O | 25 | 29 | 16 |
| 1652 | | 1632 | 4.7 | | | | | | | | $\nu_s$C–O | 23 | 22 | 25 |
| 1427[d] | 22 | 1437 | 66 | | | | | | | | | | | |
| 1401 | 490 | 1415 | 388 | $B_2$ | 1406 | 598 | 1412 | 491 | 1392 | 858 | $\nu_a$C–O | 68 | 66 | 58 |
| 1381 | 7.4 | 1410 sh | | | | | | | | | $\nu_a$C–C | 17 | 18 | 21 |
| | | 1395 | 5.9 | | | | | | | | $\beta$R | 13 | 13 | 13 |
| 1342 sh | | | | | | | | | | | $\beta_a$OH | 82 | 82 | 77 |
| 1336 | 74 | 1353 | 62 | $B_2$ | 1321 | 55.8 | 1325 | 70 | 1303 | 8.8 | $\beta_a$C–O | 11 | 10 | |
| 1312 | 202 | 1329 | 258 | $A_1$ | 1303 | 173 | 1301 | 174 | 1319 | 125 | $\beta_s$OH | 61 | 63 | 50 |
| 1301 | | 1313 sh | | | | | | | | | $\nu_s$C–O | 19 | 17 | 19 |
| 1290 | | 1305 | | | | | | | | | $\nu_s$C–C | 13 | 13 | 20 |
| 1087 | 98.5 | 1089 | 63 | $A_1$ | 1073 | 117 | 1071 | 118 | 1105 | 286 | $\beta_s$OH | 32 | 29 | 38 |
| | | | | | | | | | | | $\nu_s$C–C | 30 | 34 | 32 |
| | | | | | | | | | | | $\nu C_3=C_4$ | 29 | 29 | 19 |
| 988 | | 1009 | | | | | | | | | | | | |
| 985 | 123 | 998 | 81 | $B_2$ | 980 | 49.5 | 973 | 70 | 992 | 70 | $\nu_a$C–C | 48 | 46 | 47 |
| | | 990 | | | | | | | | | $\beta_a$C=O | 15 | 15 | 14 |
| | | | | | | | | | | | $\nu_a$C–O | 13 | 15 | 15 |
| | | | | | | | | | | | $\beta_a$OH | 13 | 12 | 13 |
| 975 | 14.8 | 970 | 15 | $A_1$ | 969 | 40.4 | 965 | 32 | 1005 | 25 | $\nu C_1-C_2$ | 39 | 38 | 35 |
| | | | | | | | | | | | $\beta_s$C=O | 29 | 28 | 22 |
| | | | | | | | | | | | $\nu_s$C–O | 13 | 15 | 20 |
| | | | | | | | | | | | $\nu_s$C–C | 12 | | |
| 951 | 10 | | | | | | | | | | | | | |
| 874 | 15 | | | | | | | | | | | | | |
| 784 | 5 | 790 | 7 | $B_2$ | 771 | 8.7 | 758 | 9.3 | 770 | 8.9 | $\beta_a$C=O | 60 | 59 | 59 |
| | | | | | | | | | | | $\beta_a$C–O | 35 | 35 | 35 |
| | | | | $A_2$ | 682 | 0 | 659 | 0 | 635 | 0 | $\gamma_a$C=O | 88 | 93 | 87 |
| | | | | | | | | | | | $\tau$R | 17 | 13 | 12 |
| 661 | 34 | 669 | 22 | $A_1$ | 661 | 21 | 650 | 21 | 657 | 32 | $\nu_s$C–C | 34 | 32 | 37 |
| | | | | | | | | | | | $\nu_s$C–O | 24 | 25 | 26 |
| | | | | | | | | | | | $\nu C_1-C_2$ | 24 | 24 | 21 |
| | | | | | | | | | | | $\nu C_3=C_4$ | 10 | 11 | |

Table 3 (continued)

| Experimental | | | | | Theoretical | | | | | | PEDs | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ar matrix | | $N_2$ matrix | | Symmetry | DFT(B3-LYP)[a] | | M2[b] | | HF[c] | | | | | |
| $\tilde{\nu}$ (cm$^{-1}$) | $I$ (a.u.) | $\tilde{\nu}$ (cm$^{-1}$) | $I$ (a.u.) | | $\tilde{\nu}$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\tilde{\nu}$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | $\tilde{\nu}$ (cm$^{-1}$) | $A$ (km mol$^{-1}$) | Vibration | DFT (%) | MP2 (%) | HF (%) |
| | | | | $B_2$ | 597 | 0.22 | 582 | 0.9 | 592 | 1.1 | $\beta R$ | 77 | 77 | 77 |
| | | | | | | | | | | | $\nu_a C-O$ | 15 | 15 | 16 |
| | | | | $B_1$ | 569 | 0.19 | 549 | 0.5 | 558 | 9.9 | $\gamma_s C=O$ | 50 | 51 | 55 |
| | | | | | | | | | | | $\gamma_s C-O$ | 47 | 47 | 46 |
| | | | | $A_2$ | 548 | 0 | 472 | 0 | 425 | 0 | $\gamma_a C-O$ | 103 | 65 | 113 |
| | | | | | | | | | | | $\tau_a OH$ | | 51 | 13 |
| | | | | | | | | | | | $\gamma_a C=O$ | | | 12 |
| 463 | 291 | 527 | 157 | $B_1$ | 490 | 277 | 486 | 279 | 402 | 328 | $\tau_s OH$ | 97 | 98 | 101 |
| 454 | | 504 sh | | | | | | | | | | | | |
| | | | | $A_2$ | 460 | 0 | 446 | 0 | 368 | 0 | $\tau_a OH$ | 93 | 50 | 87 |
| | | | | | | | | | | | $\gamma_a C-O$ | | 61 | 15 |
| | | | | $A_1$ | 293 | 0.57 | 283 | 0.09 | 304 | 1.8 | $\beta_s C=O$ | 42 | 42 | 48 |
| | | | | | | | | | | | $\nu C_1-C_2$ | 30 | 29 | 26 |
| | | | | | | | | | | | $\beta_s C-O$ | 20 | 21 | 18 |
| 254[e] | | 266[e] | | $B_2$ | 245 | 22.3 | 228 | 20 | 259 | 24 | $\beta_a C-O$ | 45 | 46 | 45 |
| 250[e] | | | | | | | | | | | $\nu_a C-C$ | 29 | 28 | 27 |
| | | | | | | | | | | | $\beta_a C=O$ | 24 | 24 | 25 |
| | | 234[e] | | $B_1$ | 211 | 6.5 | 208 | 5 | 226 | 11.2 | $\gamma_s C-O$ | 54 | 54 | 55 |
| | | | | | | | | | | | $\gamma_s C=O$ | 46 | 46 | 45 |
| | | | | $A_1$ | 206 | 12.9 | 186 | 12 | 218 | 12.4 | $\beta_s C-O$ | 68 | 68 | 70 |
| | | | | | | | | | | | $\beta_s C=O$ | 27 | 27 | 24 |
| | | | | $A_2$ | 111 | 0 | 95 | 0 | 88 | 0 | $\tau R$ | 94 | 114 | 129 |
| | | | | | | | | | | | $\gamma_a C=O$ | 13 | | |

The integral intensities are normalized in such a way, that the sum of integral intensities of all experimentally observed normal modes was equalized to the sum of the absolute intensities obtained in DFT calculations.

[a] Wavenumbers scaled down by 0.98.

[b] Wavenumbers scaled down by 0.96.

[c] Wavenumbers scaled down by 0.90.

[d] Band due to association.

[e] The spectral positions of these bands are not certain because of their low intensities.

### 4.3. Photochemical reaction

Squaric acid isolated in Ar matrix was irradiated by the light from high-pressure mercury lamp HBO 200 passed through the water filter fitted with quartz windows. After 10 min of irradiation the initial spectrum of squaric acid disappeared and a series of new absorption bands appeared. The spectra obtained after irradiation are in full agreement with the results reported recently by Maier and Rohr [18], who irradiated squaric acid isolated in Ar matrix with the light from low-pressure mercury lamp. We followed the interpretation of the spectra given by these authors and on the basis of comparison of IR spectrum of irradiated matrix with the spectra theoretically (MP2/6-31G*) predicted [18] for several possible photoproducts, we were able to identify two products: deltic acid in the conformation of $C_{2v}$ symmetry and ethynediol.

## 5. Note added in proof

The theoretical simulations of vibrational spectrum of squaric acid were also performed at the MP2/6-311 + +G** level. Application of the basis set augmented with diffusion functions should allow for better description of the system with intramolecular hydrogen bond. Nevertheless, the obtained theoretical spectra (with frequencies scaled down by the factor of 0.975) are very close to those resulting from the MP2/6-31G** calculations presented in the paper. The results of MP2/6-311 + +G** calculations are available upon request.

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