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Vibrational spectroscopy of triacetone triperoxide (TATP): Anharmonic fundamentals, overtones and combination bands

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ABSTRACT

The vibrational spectrum of triacetone triperoxide (TATP) is studied by the correlation-corrected vibrational self-consistent field (CC-VSCF) method which incorporates anharmonic effects. Fundamental, overtone, and combination band frequencies are obtained by using a potential based on the PM3 method and yielding the same harmonic frequencies as DFT/cc-pVDZ calculations. Fundamentals and overtones are also studied with anharmonic single-mode (without coupling) DFT/cc-pVDZ calculations. Average deviations from experiment are similar for all methods: 2.1–2.5%. Groups of degenerate vibrations form regions of numerous combination bands with low intensity: the 5600–5800 cm⁻¹ region contains ca. 70 overtones and combinations of CH stretches. Anharmonic interactions are analyzed.

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1. Introduction

Triacetone triperoxide (TATP), an improvised explosive, has received considerable attention in recent chemistry publications [1]. The interest is partly in the analytical chemistry of the material, and in the physical properties that may lead to new identification and characterization methods, due to the prevalent use of TATP among terrorists [2]. Other studies have dealt with the mechanism of TATP decomposition [3,4].

Among the methods for analysis of TATP that appear in the literature are: ion mobility spectrometry [5]; cavity-ringdown spectroscopy [6]; liquid chromatography with infrared detection [7]; and desorption electrospray ionization mass spectrometry [8]. Although some methods may be capable of distinguishing TATP from other peroxides, the development of new, more sensitive and convenient methods based on infrared or Raman detection of TATP may offer an alternative [1,9]. However, the fundamental vibrational frequencies of TATP appear in the same spectral region as those of detergents containing peroxides [10].

Overtone and combination bands may offer advantageous possibilities in this respect, for TATP, as well as for other molecules of interest. In principle, these transitions add considerable uniqueness and richness to the spectroscopic fingerprints of a molecule. One reason for this is the fact that overtone band intensities are dependent upon the anharmonic properties of the potential surface, and non-linear changes in the dipole moment with respect to the normal mode coordinate [11]. Similarly, combination band intensities depend upon mode coupling and coupled dipole effects. Overtone and combination bands can appear in both the infrared and nearinfrared regions. High overtones can appear in the visible region of the spectrum.

Since overtone and combination band spectra can only be calculated by using an anharmonic method, we have used vibrational self-consistent field (VSCF) methods in this work [12–14]. The VSCF method, at the simplest level, does not make assumptions about the form of the potential, but assumes that the total wavefunction for the system is a product of single-mode wavefunctions. The GAMESS program code [15,16] which was used in the present work, assumes that the potential can be truncated to include only single-mode ($V(Q_i)$) and two-mode ($V(Q_i, Q_j)$) terms. The single-mode terms (diagonal) describe the potential as a function of one vibrational coordinate, and the two-mode (coupling) potential terms describe the potential as a function of two vibrational coordinates. The two-mode terms provide information about mode coupling strengths which can aid in understanding experimental linewidths and intramolecular vibrational energy

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flow. Both the diagonal and coupling terms can affect the frequency.

The inclusion of mode–mode coupling (pairwise coupling of modes) for TATP is a substantial computational challenge, since there are 93 vibrational modes for TATP leading to a possible 4278 (= $93 \times 92/2$) coupling terms; for the combination band calculation, the same terms are also needed. Thus, in order to generate the potential surface for the complete combination band calculation, we used a method that is based on adapting the surface generated by the semi-empirical PM3 method [17,18]. We have found that this method can lead to accurate results while saving on computational effort [19,20]. In the methods section below, we briefly provide further details about the VSCF methods and potential surfaces that were used. Results of frequency data as compared to experiment, regions of possible combination band and overtone activity, and mode coupling data are described below.

2. Theoretical methods

As described above, the VSCF algorithm initially assumes that the overall wavefunction is a product of single-mode wavefunctions.

$$\Psi^{(n)}(Q_1, \dots, Q_N) = \prod_{j=1}^N \psi_j^{(n)}(Q_j)$$
(1)

In addition, the potential has been truncated to include only singe-mode and double-mode terms.

$$V(Q_1, \dots, Q_N) = \sum_{j=1}^{N} V_j^{\text{diag}}(Q_j) + \sum_{i}^{N} \sum_{i < j}^{N} V_{ij}^{\text{coup}}(Q_i, Q_j)$$
(2)

All calculations in the present work were performed by using the GAMESS suite of programs [15,16]. The GAMESS code directly calculates potential energy surface points on a grid, according the computational method chosen (e.g. DFT, PM3) for use in the anharmonic frequency calculation. Several improvements have previously been implemented into the VSCF code, and they are used here [12–14,21]. Correlation-corrected VSCF (CC-VSCF) includes correlation between the vibrational modes, and is analogous to MP2 perturbation theory calculations in electronic structure theory. First-order degenerate perturbation theory calculations that are described here are analogous to using configuration interaction within a degenerate perturbation theory is abbreviated DPT2-VSCF.

Three sets of calculations were performed: (a) using the DFT-B3LYP/cc-pVDZ method, without mode–mode coupling; (b) using adjusted PM3 surfaces, and including coupling; and (c) a partial calculation of some coupling terms at the RHF/3-21G level, in order to obtain more precise intensity information. Two conformers of TATP have previously been reported [22]: the lowest energy conformer was used in this work.

2.1. DFT

Initially, the DFT-B3LYP/cc-pVDZ [23–26] harmonic vibrational calculation that was performed previously [3,10] with GAUSSIAN98 [27], was repeated because it was found that apparently since the normal mode coordinates within each degenerate set are not unique, they differ between the two program suites. Fundamental vibrations and overtones at the DFT-B3LYP/cc-pVDZ level were obtained by using a single-mode (without coupling) 16-point grid VSCF calculation [12].

2.2. Adjusted PM3

Adjusted PM3 semi-empirical surfaces [19] were used in order to perform 16-point grid VSCF, CC-VSCF, VCI-VSCF and DPT2-VSCF calculations [12–14], which include single-mode and coupling (double-mode) terms. The adapted surfaces were obtained as follows: (1) initially, a harmonic frequency calculation at the PM3 level was performed on TATP; (2) the normal modes of TATP at the DFT and PM3 levels were compared; (3) factors were obtained for each normal mode

$$\lambda_i = \frac{\omega_i^{\text{B3LYP}}}{\omega_i^{\text{PM3}}};\tag{3}$$

(4) the factors from (3) were used to generate an adapted surface where

$$V_{\text{PM3}}^{\text{adjusted}}(Q_1, \dots, Q_N) = V_{\text{PM3}}^{\text{standard}}(\lambda_1 Q_1, \dots, \lambda_N Q_N).$$
(4)

All PM3 surfaces were scaled. (For some of the normal modes, the correspondence between the two types of calculations is ambiguous, primarily due to degeneracy. However, in general, this does not significantly change the scaling factors.) The surface was also used in order to perform calculations of overtones at the CC-VSCF level, and calculations of combination bands. A combination band code that has recently been included in the GAMESS suite of programs was used [15,16,28].

2.3. RHF/3-21G

Since the intensities obtainable by the PM3 code have not yet been adjusted, another set of calculations was performed in order to obtain more reliable intensities: the additional calculations were performed at the RHF/3-21G level [29,30]. Initially, a harmonic RHF/3-21G vibrational frequency calculation was performed on TATP, and then two partial VSCF and combination band calculations were performed. One calculation included the 36 CH stretching and CH₂ bending modes; a second calculation included 45 bending modes whose harmonic frequencies range from 800 to 1700 cm⁻¹. An 8-point grid was used and interpolated to 16-grid points using a program provided by Chaban [28]; the interpolation program relies on code found in Numerical Recipes [31]. Similarity between the normal modes was used as the criterion for applying the calculated RHF/3-21G intensities to the VSCF-adapted PM3 frequency calculations.

3. Results

3.1. Vibrational spectra of fundamentals

The structure of TATP is illustrated in Fig. 1. Several authors have studied the IR and Raman spectra of TATP [5,10,32,33], and we have compared their experimental data to the calculated values. The results are presented in Table 1. Since the measurements were done in solution or solid phase, degenerate bands are indistinguishable (also, see the coupling Section 3.3). Consequently, in order to compare our calculations, averages of groups of calculated degenerate frequencies were compared to average experimental frequencies for each band. Intermolecular interactions in solid TATP are expected to be weak: the TATP crystal structure lacks CH \cdots O interactions, TATP is volatile, and its density is lower than diacetone diperoxide (DADP) [3]. Thus, although the frequencies that are calculated here are suitable for the gas-phase, environmental effects on the measured frequencies are expected to be modest.

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Table 1

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Average calculated frequencies, compared to average experimental values

Average experimental frequency	Lines in average	Calculated frequencies				Normal mode description
		DFT harmonic	CC-VSCF	VCI-VSCF	DFT, VSCF diag	
555	2	546.4	558.1	558.2	545.2	00C b, CCO b, CCOO t
555	1	555.8	567.4	568.0	555.2	OCO b, ring expansion
597	1	572.7	571.8	571.8	572.5	COOC t
617	2	623.3	627.5	627.5	622.6	OCO b, COOC t
785	2	790.8	781.8	782.7	791.3	OCOO sh, CCO sym str
816	1	843.9	850.4	851.5	844.2	CO str, CCCO sh
842	2	889.1	893.6	895.1	888.6	OCOO sh
863	3	905.5	908.3	908.2	907.6	OO str
885	1	853.9	844.9	848.0	852.5	CCO sym str
937	3	938.5	950.5	952.5	941.1	CCO b, CCC str
946	2	957.8	965.2	967.1	956.0	CO str, OCO b, CCC b
946	1	963.6	970.7	971.3	961.0	CCC b, OCO b, CO str
1008	2	1007.5	1014.4	1016.6	1006.9	OCO b, CCC str, COOC t
1018	1	1026.5	1033.9	1036.6	1023.4	COOC t, CO str, CH ₃ str
1129	1	1137.4	1115.7	1116.4	1134.8	CCO b, CO str
1186	2	1196.6	1176.5	1177.4	1194.9	CC str, CCO b
1202	2	1215.0	1195.6	1196.4	1212.8	CCC b, OCO b
1234	1	1248.1	1227.1	1227.8	1248.3	CC str, CCO b
1246	1	1222.3	1202.5	1204.4	1219.8	OCOb, CO str
1275	2	1288.7	1263.7	1264.7	1288.3	CCO b, CO str
1369	1	1355.7	1328.7	1330.2	1366.3	CCC asym str
1369	2	1377.0	1349.6	1349.7	1379.2	CCO b
1386	3	1387.4	1357.0	1359.5	1388.4	CCC sym str
1434	3	1441.1	1404.4	1403.3	1441.4	CH ₂ b
1448	6	1455.0	1416.1	1416.3	1456.2	CH ₂ b
1460	3	1478.2	1438.1	1436.9	1476.4	CH ₂ b
2718		overtone and/or c	ombination			
2867	3	3055.7	2814.6	2824.6	3058.4	CH str
2948	3	3061.1	2789.4	2843.4	3034.8	CH str
2997	3	3156.6	2936.6	2950.2	3165.2	CH str
3004	3	3136.6	2907.6	2933.9	3210.4	CH str
3004	3	3163.7	2943.0	2956.0	3152.3	CH str
3004	3	3146.4	2916.0	2932.3	3183.0	CH str

Experimental values are averages of data from Refs. [5,10,32,33].



Fig. 1. Structure of the TATP conformer used in the present work.

The average deviations of the calculations from the experimentally measured lines are presented in Table 2, and a selection of the spectrum $(1000-1300 \,\mathrm{cm}^{-1})$ is shown in Fig. 2. The harmonic DFT calculations were not multiplied by a factor, as is frequently done: however, the DFT harmonic frequencies of the bends and torsions are very close to experiment, and this is assumed to be due to fortuitous shallowness of the DFT potential surfaces. Large deviations for DFT harmonic frequencies were obtained in the CH stretching region $(3000 \,\mathrm{cm}^{-1})$. Of the anharmonic calculations, the VCI-VSCF method yields frequencies that are most consistently close to experimental results.

Two regions of the spectra were particularly difficult to assign: the CH stretching region (3000 cm^{-1}) and the CO and OO stretching region (near 780–950 cm⁻¹). The experimental IR spectrum [32] shows two strong peaks near 3000 cm^{-1} that are separated by less than 10 cm^{-1} and a third small peak near 2950 cm^{-1} , while the calculations indicate that the two most strongly absorbing triplets of lines are separated by 85–150 cm⁻¹. The discrepancy may be due to the fact that there are 18 degenerate CH stretches, which are best calculated with a method that accounts for the degeneracy such as VCI-VSCF method. In the CO and OO stretching region, the calculated frequency order of

Table 2

Average deviations (in absolute percentages) of the calculations from experimentally measured values [5,10,32,33]

	DFT harmonic	Adapted PM3 CC-VSCF	Adapted PM3 VCI-VSCF	DFT, VSCF single mode
CH stretches	5.04	2.90	2.15	5.50
Bends/torsions	1.37	2.12	2.13	1.38
Overall	2.33	2.32	2.14	2.45



Fig. 2. Stick spectrum comparison of the VCI-VSCF and DFT harmonic frequencies, with experimental data taken from Ref. [5] (maximum peak heights were converted to absorbances and scaled).

the modes and the IR and Raman intensities differ from experiment. The experimental assignments in this region were based on the tentative assignments of Buttigieg et al. [5]. Since the PM3 surface was adapted according to the DFT frequencies, flaws in the DFT potential will also affect the adapted PM3 calculation. Additionally, the deviations from experiment may reflect the fact that the calculations were performed on an isolated TATP molecule, and intermolecular interactions are not accounted for.

3.2. Combination bands and overtones

As mentioned above, the intensity of overtones and combination bands, is generally due to anharmonicity of the potential surface and/or non-linear terms in the dipole moment function. For TATP, the number of possible one-plus-one combination bands is nearly 4300, and this number does not include hot bands. Thus, the TATP spectrum is very rich, and it is possible that the combination bands of TATP may also provide a more unique means of identification than the fundamental IR spectrum. For example, a combination band due to a OO or CO stretching mode combined with a CH stretching or CH₂ bending mode may be observed for an organic peroxide, but not for the types of peroxides that are added to laundry detergents [10].

A summary of the combination bands whose intensities are greater than, or equal to, 0.05 km/mol is given in Table 3. Combination band intensities are much weaker than the fundamentals; for example, the TATP CH stretching fundamental intensities are calculated to be ca. 5-20 km/mol (VSCF/DFT) and bending modes with very strong intensities, have calculated intensities of ca. 100-200 km/mol. (Note that overtone spectra of alkane CH stretches in the literature indicate that overtones which have oscillator strengths that are a factor of 2000-10000 less than the fundamentals can be measured [34].) Combination bands of the OO stretching modes are given separately in Table 4. Examination of the calculated data in Table 3 indicates that there are regions of the spectrum in which sets of degenerate, or nearly degenerate, modes form combination bands with similar frequencies. In the bending and torsional region, the number of modes comprising each degenerate, or nearly degenerate set, is smaller; often the

modes are in groups of single lines, doublets or triplets. Groups of such modes falling within similar spectral regions that are comprised of similar motions of atoms (e.g. CCO bending) nonetheless lead to clusters of combination band absorptions with similar frequencies.

Combinations of the 18 CH stretching modes comprise roughly half of the combination bands listed, and since previous work [19] has shown that the potential along a stretching mode can have a high degree of anharmonicity, the abundance of combination bands of CH stretches with non-zero intensity is not surprising. Additionally, many of the CH stretch fundamentals have strong intensities, so that the combination bands are also thought to have non-zero intensities due to the large change in the dipole moment with respect to the normal mode. The combination bands of the CH stretching modes show gaps in frequencies, which arise from the frequency differences of the calculated fundamentals. Since the measured fundamental vibrational spectra show a smaller frequency gap than that which is calculated, it is expected that experimentally measured combination bands would also have smaller frequency gaps. For identification purposes, the CH stretching combination bands in the 5600–5900 cm⁻¹ region (due to CH stretches alone) may not be unique since many materials possess methyl groups. Combination bands in regions from 3667 to 3866 cm^{-1} and 4130 to 4300 cm^{-1} , due to combinations of CH stretches with CCO bending and CCC stretching modes, may be helpful for identification since fewer molecules have structures that would lead to CCC stretching and CCO bending modes.

Although the lines due to combinations of individual modes may have intensities that are too low to measure, some groups of combinations of degenerate modes may be observed due to their overlap. In fact, the literature spectrum of Bellamy [32] shows several very low intensity bands in the 2000–2300 cm⁻¹ region and near 3300–3700 cm⁻¹ which may possibly be due to overtones and combination bands. Additionally, since the combination band intensities calculated near 2000–2300 cm⁻¹ were primarily calculated at the RHF/3-21G level and those near 3300–3700 cm⁻¹ were calculated with PM3, they are less accurate than those obtainable from higher level calculations. A stick spectrum of the overtones (VSCF/DFT intensities) and combination bands in the 1500–3000 cm⁻¹ region, is given in Fig. 3.



Fig. 3. Stick spectrum of overtones and combination bands from 1500 to 3000 cm⁻¹.

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Combination bands with intensities greater than, or equal to 0.05 km/mol

Frequency region (cm ⁻¹) CC-VSCF/adapted PM3	Number of lines int. \geq 0.05 km/mol	Mode Type 1	Mode Type 2
5609–5623, 5670–5900 4184–4227, 4312–4377 4131–4171, 4240–4307 3667–3866 2907–3251	3, 53 17, 44 9, 39 11ª ≥21 ^b	CH str	CH str CH ₂ bend CCO b, CCC str OCO b, CCO b, CO str, COOC t, OCOO sh ring modes, low freq tors
2802-2856	5	CH ₂ bend	CH ₂ bend
2675–2720	9	CCO b, CCC str	CCO b, CCC str
2554-2649, 2676-2702 2469-2478, 2533-2628 2489-2527	22, 6 3, 13 3	CH ₂ bend CCO b, CCC str OCO b, CCO b, CCC b, CO str, CC str	OCO b, CCO b, CCC b, CO str, CC str
2289, 2290, 2331–2453 2134–2140, 2175–2387 2008–2193, 2226, 2351 1796–1914, 2050, 2055	1, 1, 35 4, 43 15 ^c , 1, 1 7 ^c , 1, 1	CH ₂ bend CCO b, CCC str OCO b, CCO b, CCC b, CO str, CC str OCO b, CCO b,CO str, COOC t, OCOO sh	OCO b, CCO b, CO str, COOC t, OCOO sh
1158, 1225, 1568, 1628 598, 720, 983, 1008, 1109	1, 1, 2, 3 ^b 2, 2, 2, 3, 2 ^b	Varied	Ring modes, low freq. tors

Intensities were calculated with RHF/3-21 G, unless noted otherwise.

^a Based on PM3 intensity.

^b Based on PM3 intensity, some torsions excluded due to choice of coordinates.

^c OO stretching combinations appear in this region, and are shown in Table 4.

Since OO stretching modes can characterize the peroxides, data for their combination bands is given in more detail in Table 4. The fundamental OO stretching bands are not observable in the IR, but are observable by Raman spectroscopy near $866 \,\mathrm{cm^{-1}}$ [5]. The calculated IR intensity of these combination bands is significant; it is based upon a two-dimensional integral of the dipole function, and is taken over a range of geometries. The strongest combination bands are calculated to appear near 2021 and 2133 cm⁻¹, and they are doublets, due to the degeneracy of the asymmetric OO stretches. There are also a number of combination bands in this region that are due to CCO bending motions and these may also offer a means of identification for TATP.

The overtones with the strongest intensity are listed in Table 5. Again, as with the combination bands, many of the stronger overtones arise from CH stretching modes. Since CH stretching modes are common to many organic molecules, they cannot be the sole means of identifying TATP. As shown in Fig. 3, some of the overtones due to CCC stretches and CCO bends appear in the region near $2700 \,\mathrm{cm^{-1}}$; these absorptions may be useful for identification purposes. Second overtones of these same vibrations have stronger intensities than other overtones, and they may or may not be significant (0.01–0.03 km/mol according the VSCF/DFT-B3LYP); their frequencies are from 4047 to 4073 cm⁻¹ (CC-VSCF/adapted PM3).

Table 4

Combination bands of OO stretching modes

Overall, the region from 2000 to 2900 cm^{-1} appears to be suitable for identification of TATP, since the absorptions in that region are characteristic and they do not overlap with other bands. Additionally, it is a region in which detectors are available. The region from 4100 to 4300 cm^{-1} is also suitable with detection by photoacoustic spectroscopy. The existence of a large number of combination bands in a narrow spectral region, however, could lead to fast vibrational energy transfer which may affect the linewidths and intensities. Consequently, lines were also sought that: may be characteristic of TATP; that are separated from the other combinations in the same group of bands (by approximately 5–10 cm⁻¹); that are separated from fundamentals; and that have significant intensity. Such bands were found (from CC-VSCF/adapted PM3) at: 1822, 2055, 2478, 2649, 2728 and 4171 cm⁻¹.

3.3. Mode coupling

Coupling between an individual pair of modes was characterized by the quantity defined in Eq. (5), and which was computed by numerical integration; Q_i and Q_j are the normal mode coordinates for modes *i* and *j*.

$$\mathcal{I}_{ij} = \langle \psi_i(Q_i)\psi_j(Q_j)||V_{ij}(Q_i, Q_j)||\psi_i(Q_i)\psi_j(Q_j)\rangle$$
(5)

combination bands of oo stretching modes			
Frequency (cm ⁻¹) CC-VSCF/adapted PM3	Mode combined with OO stretch	Intensity (km/mol) (rhf/3-21g)	
2242	CCC asym str	0.07	
2175, 2177 2171 (2 lines) 2168 (2 lines)	CCO b, CO str	0.18, 0.18 0.08, 0.07 0.08, 0.08	
2140 2133 (2 lines)	CC str, CCO b	0.1 0.38, 0.38	
2028 2021 (2 lines)	CCO b, CO str	0.17 0.6, 0.6	
1925, 1930 1756 (2 lines) 1225	OCO str, CCC str, COOC t CO str, CCCO sh COOC tors	0.05, 0.05 0.08, 0.08 0.2 ^a	

^a PM3 intensity.

Mode description	Frequency (cm ⁻¹) CC-VSCF/adapted PM3	Intensity (km/mol) VSCF/B3LYP/DFT	
	5877.85	0.48	
	5861.35	0.52	
	5857.27	0.41	
	5851.38	0.49	
	5797.15	0.35	
	5796.34	0.52	
	5790.54	1.09	
CH str	5785.97	1.01	
	5784.11	1.05	
	5781.5	0.92	
	5770.35	0.91	
	5761.82	1.14	
	5611.46	0.1	
	5609.01	0.11	
	5567.17	0.24	
	2842.94	0.07	
CII band	2838.03	0.07	
CH ₂ Della	2832.99	0.1	
	2814.09	0.06	
	2722.6	0.33	
CCC sym str	2710.48	0.25	
	2704.54	0.32	
660 I I	2703.17	0.25	
CCO bend	2691.93	0.22	
CCC asym str	2656.66	0.34	
CCO h CO et a	2527.55	0.08	
CCO D, CO SIF	2522.96	0.08	
OCOO sh	531.46	0.06	

Table 5

with intensity > 0.05 km/mol

Note that ground state wavefunctions are used here, and the use of an excited state wavefunction could increase the value of the integral since it would be centered further from the equilibrium geometry. As found in previous work [19], very strong coupling exists between CH stretching modes. The coupling between the CH stretches is illustrated in Fig. 4, where the shading of each square corresponds to the amount of coupling between the modes indicated on the axes. As can been observed, there is strong coupling between several of the modes and most of the



Fig. 4. Coupling between CH stretching modes. Each square is shaded according to the value of the coupling integral in cm^{-1} , and the VCI-VSCF frequencies in cm^{-1} for the modes are indicated on the axes.



Fig. 5. Coupling between modes in the CO stretching region. Each square is shaded according to the value of the coupling integral in cm^{-1} , and the VCI-VSCF frequencies in cm^{-1} for the modes are indicated on the axes.

other CH stretches, this is seen in particular for the modes at 2834, 2842 and 2855 cm⁻¹. The maximum value for the coupling among CH stretches in TATP is 106 cm^{-1} , for coupling between a symmetric CH₃ stretch centered on two methyl groups, and a symmetric CH₃ stretch centered on all six methyl groups (thus overlapping with the coupled mode) and which have VCI-VSCF frequencies of 2820 and 2842 cm⁻¹, respectively. As discussed in Section 3.1, it is difficult to assign the calculated vibrations to the experimental frequencies in this region: strong coupling between modes could explain the differences in intensity between the two.

Coupling to torsional modes also is strong, however, these will not be discussed here since normal mode coordinates (which were transformed to Cartesians) were used in the present calculations and torsional coordinates are preferred over use of normal mode coordinates for torsional mode analyses [35]. Coupling between two of the CH stretching modes and several modes containing CCC bends and stretches, CCO bends and stretches, COOC torsions and OCOO shearing in the 850–1037 cm⁻¹ range is strong, ranging from 15 to 24 cm^{-1} .

A coupling diagram for modes in the region $965-1266 \text{ cm}^{-1}$ containing CO and OO stretches (according to the VCI-VSCF calculations) is given in Fig. 5. As shown in the chart, there appears to be significant coupling among the modes in this region. For example, three modes in the region $1195-1204 \text{ cm}^{-1}$ (comprised of two which are CCC and OCO bending modes, and an OCO bending and CO stretching mode) are moderately coupled to most of the modes



Fig. 6. Integrated coupling of a selection of modes to a mode containing and OCO bend and a CO stretch, shown in the inset. Frequencies are from VCI-VSCF.



Fig. 7. Coupling between modes in the OO stretching region. Each square is shaded according to the value of the coupling integral in $\rm cm^{-1}$, and the VCI-VSCF frequencies in cm⁻¹ for the modes are indicated on the axes.

in the 965–1266 cm⁻¹ range: most of the couplings range from 1 to 12.5 cm⁻¹. Also shown in Fig. 5, is a COOC torsion, CO stretching and CH₃ stretching mode with frequency 1037 cm⁻¹. This mode has moderate coupling to the modes in the range of $1014-1266 \text{ cm}^{-1}$. Fig. 6 shows a chart with values of the integrated coupling of the mode at 1204 cm⁻¹ with several other modes; it is, in general, more strongly coupled to others in the same frequency range. Overall, the number of vibrations and the extent of their coupling in this region could lead to rapid vibrational energy redistribution and wider linewidths, possibly causing difficulty in high-resolution gas-phase measurements.

Coupling in the region of the OO stretches is shown in Fig. 7. According to the VCI-VSCF calculation, the OO stretching frequencies are: 906, 906 and 913 cm⁻¹. They are strongly coupled together, with coupling between the totally symmetric mode and the asymmetric modes being 12 cm^{-1} , and coupling between the asymmetric modes being 9 cm^{-1} . The figure also shows that there is strong coupling among CCO stretching modes with frequencies of 782, 783 and 848 cm⁻¹, and the CCO stretching modes are strongly coupled to other nearby modes. The extensive coupling in this region could explain difficulties in frequency assignments, and could lead to wider experimental linewidths.

4. Conclusions

Anharmonic vibrational calculations have shown that the vibrational spectrum of TATP is rich with many combination bands with intensities that are weak but may be measureable. Extensive coupling between modes exists in the CH, CO and OO stretching regions of the spectrum. Thus, although the use of fundamental vibrations for identification of TATP may be difficult for unique identification, the use of overtones and combination bands may be advantageous. The spectral regions 2000–2900 and 4100–4300 cm⁻¹ contain combination bands and overtones that may aid in identification of TATP. Calculations of vibrational spectra of molecules such as TATP could be aided by improvements in spectral simulations by consideration of strong mode coupling, and by the use of a more expensive computational methods for calculations of the dipole moments along the molecular coordinates.

Comparison of the VCI-VSCF calculations with experiment, for the transitions where data is available, is generally encouraging. An alternative to using anharmonic first-principles vibrational methods for identification purposes could be the application of empirical scaling methods for the harmonic values [36]. However, these widely used prescriptions are not available or tested for combination band transitions, and combination band transition intensities would be lacking. We therefore believe that there may be important advantages for using first-principles anharmonic vibrational calculations for identification purposes.

Finally, for issues other than identification, the VSCF method has the merit of computing the vibrational spectrum, including the anharmonic effects, from the potential surface. Therefore, the calculations shed light on anharmonic coupling between different modes, which is directly relevant to intramolecular vibrational energy flow. Thus, the VSCF spectroscopic calculations provide data that may also be relevant for understanding the dynamical properties of TATP.

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