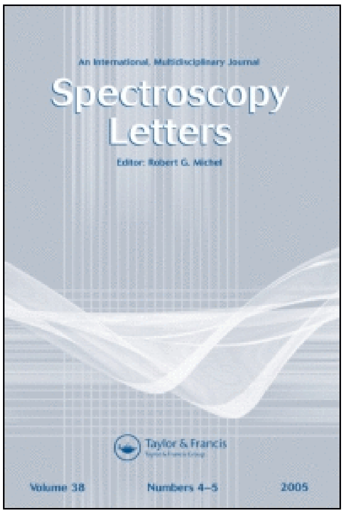

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Vibrational Spectrum of Tetramethyldioxetane

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To cite this Article Aroca, Ricardo and Menzinger, Michael(1983) 'The Vibrational Spectrum of Tetramethyldioxetane', Spectroscopy Letters, 16: 12, 945 — 951

To link to this Article: DOI: 10.1080/00387018308062404

URL: http://dx.doi.org/10.1080/00387018308062404

SPECTROSCOPY LETTERS, 16(12), 945-951 (1983)

THE VIBRATIONAL SPECTRUM OF TETRAMETHYLDIOXETANE

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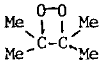
ABSTRACT: Based on Fourier transform IR and Raman spectra and on the vibrational frequencies calculated for a simplified molecular model we propose a vibrational assignment of normal modes of tetramethyldioxetane (TMDO).

Dioxetanes, particularly TMDO,  have attracted much interest because of the intense chemiluminescence accompanying their cleavage into two carbonyl compounds (1,2). That process has been initiated thermally (1, 2), by collisional activation in molecular beams (3), by electronic excitation (4) and vibrational overtone pumping (5) through photoabsorption in the visible, and by multi-photon IR absorption (6). The possibility of selectively pumping different vibrational modes (5) and of observing mode-specific reaction dynamics appears very attractive and has motivated the present spectral assignment. The results are tentative, mostly due to complications with and incompleteness of the Raman spectra, caused by laser-induced decomposition of the sample.

EXPERIMENTAL: The TMDO sample was kindly provided by Prof. K. Kopecky (7). Infrared spectra of nearly saturated solutions in n-octane were recorded on a NICOLET 7000 FT-IR spectrometer. Not previously reported far infrared spectra is shown in figs. 1. Raman spectra of TMDO solutions in CCl_4 were obtained using Ar^+ ion laser radiation (488nm). Scattered light was dispersed by a SPEX 14018

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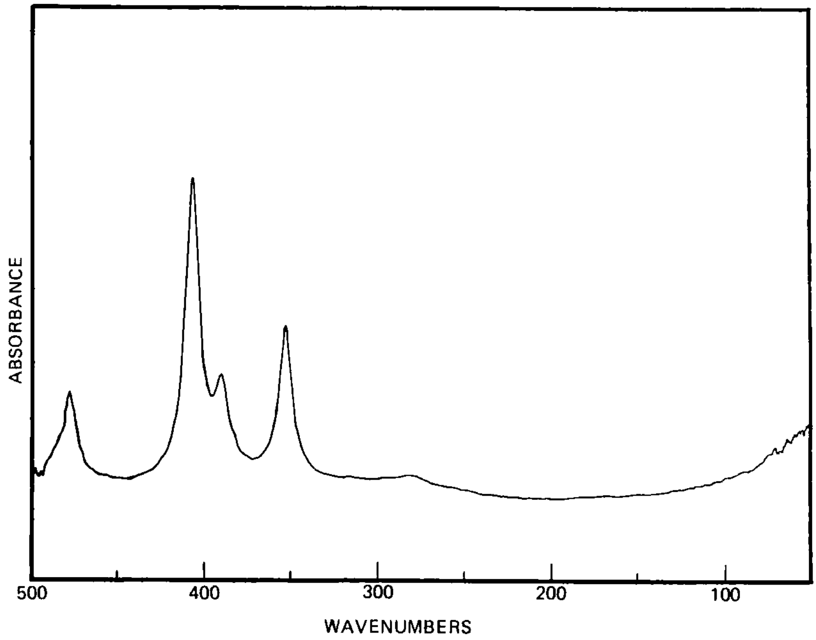

FIGURE 1

double monochromator equipped with holographic gratings and was detected by a cooled HAMAMATSU R955 photomultiplier and photon counting electronics. Laser-induced decomposition and the solvent spectra somewhat interfered with the acquisition of Raman data so that only 11 transitions could be observed. All of them were polarized. All spectral features are summarized in table 1.

INTERPRETATION OF SPECTRA: The vibrational spectrum of TMDO (20 atoms) comprises 54 normal modes. We observed only 41 distinct spectral features due to accidental degeneracies, band overlap, very weak bands and transitions outside the experimental range (< 50 cm^{-1}). Support for the empirical assignment of this partial spectrum is obtained from the vibrational frequencies, calculated (8) for a simplified molecular model based on the group force constants for similar compounds.

In the spirit of Wilson's GF method (8), each internal coordinate (bond length or angle variation) is preferentially assigned to one or more normal modes. Normal frequencies that are almost entirely related to a given internal coordinate are said to be characteristic frequencies and can be easily interpreted in series of molecules with similar structural groups. This is the case, for instance, with the 12 C-H stretching vibrations in the 2900 - 3000 cm^{-1} region. Only nine distinct spectral features are observed in this range (see table 1), probably due to accidental degeneracy and band overlap. The transitions below 2900 cm^{-1} are also assigned to fundamental $-CH_3$ stretching vibration on the basis of their high relative intensity. Among the 54 normal modes, 34 belong to deformation vibrations. Twenty of these are bending and rocking vibrations of the $-CH_3$ groups (9, 10). The H-C-H bendings are clearly located in the 1300-1490 cm^{-1} region. These bands are listed in table 1 under the general term $-CH_3$ bends. Methyl rocking vibrations are usually observed within a broad region below 1100 cm^{-1}. These vibrations are normally associated with IR and Raman bands of low intensity. Two such bands are identified in table 1 as CH_3- rock. Furthermore, the methyl groups attached to carbon atoms give rise to four low frequency torsion modes, probably below 150 cm^{-1}. Methyl group torsion vibrations are characterized by a very low value of the dipole moment and polarizability derivatives and correspondingly low infrared and Raman intensities. The fact that we do not observe identifiable torsional vibrations is therefore not surprising. Following the assignment of the CH_3-frequencies there remain 8 stretching and 10 bending vibrations related to skeletal modes. To ease the assignment of these vibrations we have carried out calculations of molecular frequencies by Wilson's GF method (8). This simplified molecular model was assumed to belong to the C_{2v} point (13) and to consist of eight mass points, with methyl groups collapsed to a single masspoint m = 15. The approximate force constants were transferred directly from hydrocarbons (11) and from cyclobutane (12), without attempting a further refinement. The resulting frequencies and potential energy distributions form the basis of the assignment of skeletal vibrations.

On this ground we assigned the IR band at 1206 cm^{-1} to the antisymmetric stretching of C-C-C groups. The band at 1172.4 cm^{-1}, which is also Raman active, is mainly related to the symmetric ring stretching vibration A_1 in which the C-C bonds participate most strongly. The symmetric ring stretching vibration involving mainly the O-O bond occurs, according to our model, at lower frequency: most probably it is the Raman band at 670 cm^{-1}. The IR band at 822 cm^{-1} was assigned to the symmetric stretch A_1 of the C-C-C group. This assignment agrees well with similar observations for acetone (9) and with our calculated value. A second antisymmetric C-C-C vibration, calculated to lie a 1133 cm^{-1}, fits well the IR band at 1135 cm^{-1}. This assignment is reasonable considering that similar transitions are known for acetone (9) at 1215 cm^{-1} and for propane (10) at 1054 cm^{-1}. The Raman and IR bands at 868 cm^{-1} could be described as a ring breathing vibration which is strongly coupled with other stretching modes. Ring breathing has been reported in cyclobutane (12) at substantially higher frequency 1001 cm^{-1}, but we do not observe a transition in this region.

Scissor vibrations of the C-C-C moieties have been seen at 369 cm^{-1} in propane and at 390 cm^{-1} in acetone, and our calculated values lie in this spectral region. Hence we ascribe the bands at 390.5 cm^{-1} and 407.1 cm^{-1} to symmetric and antisymmetric scissor vibrations, respectively. The calculation predicts the ring puckering vibration at 122 cm^{-1}, but no IR or Raman band is observed below 282 cm^{-1}. Twisting and sym-wagging of the four methyl groups is likewise expected but not observed below 282 cm^{-1}. In addition to the forementioned bands we have also tentatively assigned other transitions as C-C-C group bending and ring deformation vibrations. Their description is found in table 1.

TABLE 1

Observed wavenumbers for TMDO

FT-infrared		Raman (CCl_4 sol.)		Description
3005	m	3005	m	C-H stretch
2992	s	2995	m	"
2977	s	2975	m	"
2942	m			"
2904.4	m			"
2880.3	w			"

FT-infrared		Raman (CCl_4sol.)		Description
2869.7	w			"
2850	w			"
2834	w			"
1560	vw			Combination and overtones
1544	vw			"
1520	vw			"
1510	vw			"
1487	sh			$-CH_3$ bend
1482	sh			"
1478.5	m			"
1472.1	s			"
1468.6	s			"
1462.8	s			"
1457	m			"
1451	m			"
1446.3	s	1440	m(broad)	"
1375.2	vs			"
1320	vw			CH_3 bend
1307	w			"
1206	m			C-C-C antisym. stretch
1174.4	vs	1171	w	ring stretch
1135	vw			C-C-C antisym. stretch
982	w	982	w	(CH_3) rock
930	vw	929	w	(CH_3) rock
870	m	868	w	ring breathing
822	w			C-C-C sym. stretch
729	w			
670	vw	670	m	O-O ring stretch
626.5	w	626	w	C-C-C wagging
478.8	m			C-C-C rocking
407.1	s			C-C-C antisym. stretch

(continued)

FT-infrared		**Raman (CCl_4 sol.)**		**Description**
390.5	m	390	vw	C-C-C sym. scissors
353.4	ms			ring deformation
282	w			ring deformation

CONCLUSION: We propose a vibrational assignment of observed infrared and Raman bands of tetramethyldioxetane. TMDO spectra were obtained from solutions in n-octane and in carbon tetrachloride. Experimental difficulties in sample handling due to the high rate of decomposition, particularly under laser-irradiation have prevented us from obtaining more complete results. Therefore and because of the large size of the TMDO molecule one must consider the present assignment as tentative.

ACKNOWLEDGEMENTS

We would like to thank Prof. Kopecky for the helpful correspondence and the TMDO sample. Financial support from National Science Engineering Research Council of Canada is gratefully acknowledged.

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Received: August 16, 1983
Accepted: September 12, 1983