

## Normal Coordinate Analysis of 1,3 Dioxole-2-Thione

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**Summary:** Infrared and Raman data of 1,3 dioxole-2-one,  $CH=CH-O-C(O)-O$  (vinylene carbonate) has been analysed through a normal coordinate calculations to give a better vibrational assignment and a force field for this molecule.

## Introduction

The vibration and rotation spectra and molecular structure of a series of oxygen and sulphur containing five membered rings have been extensively studied. Much of this work has been published.<sup>1-3</sup> The vibration spectra of this molecule has been very carefully studied by earlier workers.<sup>4,5</sup> Since no normal coordinate analysis had been reported and some assignments are in need of revision. Therefore, small adjustments were decided in the allocation of modes, which depend on the force constants connected with CH groups and normal coordinate analysis was carried out.

The fundamental vibration frequencies (3N-6) of a molecule can be calculated using appropriate interatomic force constants, molecular geometry and atomic masses. An excellent explanation of the fundamental theory of normal coordinate in terms of matrix algebra is given in ref. 6, chapter 1 and 2; a brief account is presented here. In a molecule, consider N as the number of atoms, with X as the cartesian coordinate displacement and  $m^{-1/2}$  the diagonal matrix having (3N) roots of atomic mass. The mass weighted cartesian coordinate may be defined as,  $q = m^{-1/2}X$ . Let S be the internal coordinate vector, which is expressed in terms of the cartesian displacement vector by use of the B-matrix.<sup>6,7</sup>

$$B_{ij} = \delta S_i / \delta X_j \quad (1)$$

$$S = BX \text{ or } S = Bm^{-1/2}q \quad (2)$$

The expression for kinetic energy, will be

$$2T = \sum_i m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \quad (3)$$

or

$$2T = \dot{X}^+ m^{1/2} m^{1/2} \dot{X} = \dot{q}^+ 1 \dot{q} \quad (4)$$

Here + indicates the transpose of a matrix and the expression for potential energy will be

$$2V = S^+ FS \quad (5)$$

Here  $F_{ij} = \delta^2 V / (\delta S_i \delta S_j)$  are normal valence force constants, defined as,

$$f = B^+ F B \text{ and } f^q = m^{-1/2} B^+ F B m^{-1/2} \quad (6)$$

The potential energy can be written,

$$2V = X^+ f X = q^+ f^q q \quad (7)$$

It is clear then that, by using mass weighted cartesian coordinates, the kinetic energy reduces to a unit (G) matrix and thus solution of matrixes for kinetic and potential energy can give the fundamental frequencies of the system, but nevertheless for polyatomic molecules, such as the present case, the calculation of these fundamental frequencies is a very tedious job, but fortunately computer programmes have been developed recently<sup>8-10</sup> and have made the task easier. Most of them, however, differ mainly in their approach to the solution of the eigenvalue problem:  $(GF - \lambda E) L = O$  and in the least squares procedure adopted, but they all work within the Wilson GF-method<sup>7</sup> using internal symmetry coordinates. In the present investigation, a computer program

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Table 1. Observed<sup>a</sup> and calculated wavenumber values and potential energy distribution for the normal vibration of vinylene carbonate.

Normal vibration	Wavenumber values (cm <sup>-1</sup> )		Approximate potential energy distribution with-in normal vibrations*
	observed	calculated	
symmetry species A			
$\nu_1$	3176	3176	S2 (99)
$\nu_2$	1864	1883	S5 (82), B3 (10)
$\nu_3$	1632	1629	S1 (46), S4 (10) B1 (18)
$\nu_4$	1166	1184	B1 (61), S1 (14)
$\nu_5$	1097	1035	S4 (52), S1 (19) S3 (13)
$\nu_6$	881	868	S3 (56), S4 (17) S3/S3 (18)
$\nu_7$	733	723	B3 (57), S5 (11)
symmetry species A <sub>2</sub>			
$\nu_8$	1514	1515	B7 (80), B5 (20)
$\nu_9$	380	383	B5 (80), B7 (20)
symmetry species B <sub>1</sub>			
$\nu_{10}$	1335	1336	B7 (80), B7/B7 (18)
$\nu_{11}$	773	774	B8 (85), B6 (11)
$\nu_{12}$	233	234	B6 (86), B8 (10)
symmetry species B <sub>2</sub>			
$\nu_{13}$	3176	3177	S2 (98)
$\nu_{14}$	1343	1369	B1 (65), S4 (38) B4/B1 (-14)
$\nu_{15}$	1083	1174	S3 (63), B3 (20) S3/S3 (-20)
$\nu_{16}$	1029	1000	S4 (36), S3 (21)
$\nu_{17}$	716	738	B4/B1 (18) B4 (51), B3 (33)
$\nu_{18}$	534	450	B4/B1 (-34), B1 (24) B2 (49), S3 (38) S3/S3 (-22)
Inertial defects			
0	0.037	-0.112	
1	-0.390	-0.425	
2	-0.816	-0.734	
3	-1.231	-1.052	

<sup>a</sup>Wavenumber values taken from ref. 3,4.

\*Symbols represent the various force constants (table II), and figures in parenthesis are % contributions of force constants (major contributions only are included).

Table 2. Final values of force constants from least squares refinement.

Description of coordinates involved		Force constants
S1	C = C stretch	6.600 m dyne A <sup>-1</sup>
S2	C - H „	5.480 „
S3	O <sub>(1)</sub> - C <sub>(2)</sub> stretch	4.381 „
S4	O <sub>(1)</sub> - C <sub>(5)</sub> „	4.101 „
S5	C = O „	12.980 „
B1	C = C - H in plane bend	1.055 m dyne A rad <sup>-2</sup>
B2	O - C = O „ „ „	1.294 „
B3	C - O - C „ „ „	3.602 „
B4	O - C = C „ „ „	1.076 „
B5	ring bending (twist)	0.589 „
B6	ring bending (envelope)	0.100 „
B7	C - H out of plane bend	0.849 „
B8	C = O „ „ „ „	0.715 „
B7/B7	C <sub>(4)</sub> - H oop bend/C <sub>(5)</sub> - H oop bend	0.206 „
B4/B1	O <sub>(1)</sub> - C <sub>(5)</sub> = C <sub>(4)</sub> bend/C <sub>(4)</sub> = C <sub>(5)</sub> - H bend	0.701 „
B1/B1	C <sub>(4)</sub> = C <sub>(5)</sub> - H bend/C <sub>(5)</sub> = C <sub>(4)</sub> - H bend	0.154 „
S3/S3	O <sub>(1)</sub> - C <sub>(2)</sub> stretch/O <sub>(3)</sub> - C <sub>(2)</sub> stretch	1.964 m dyne A <sup>-1</sup>
S2/S2	C <sub>(4)</sub> - H stretch/C <sub>(5)</sub> - H stretch	-0.022 „
S5/S3	C = O stretch/O <sub>(1)</sub> - C <sub>(2)</sub> stretch	2.001 „
S3/B3	O <sub>(1)</sub> - C <sub>(2)</sub> stretch/C - O - C bend	0.863 m dyne rad <sup>-1</sup>

written by D. Christen,<sup>11</sup> which utilizes the Gwinn normal coordinate program<sup>12</sup> has been used; its detailed description is given elsewhere.<sup>13</sup>

#### Vibrational Spectra and Force Field Calculations:

The infrared and Raman study of vinylene carbonate has been the subject of an earlier analysis.<sup>4,5</sup> As a check, Christen's<sup>13</sup> least square refinement programme was applied to the literature data of vinylene carbonate.<sup>4,5</sup> A good general agreement with previous assignments in the allocation of modes, which depend on the force constants connected with CH groups, the over all consistency of the fit has improved. The normal coordinate calculations were carried out using valence type force constants in a basis of massweighted cartesian coordinates.<sup>14</sup> Several factors added to complicate these

calculations. Most important were the lack of data (18 measured frequencies compared to many different elements in a general harmonic force field) and the obvious strong mixing of internal vibrational modes, which resulted in highly significant contributions to the Jacobian matrix from several interaction constants. This mixing was also responsible for drastic changes in the vibrational energy distribution ("assignment") upon minute changes in interaction constants. Thus a "reasonable" energy distribution was used as an extra criterium to decide the goodness of a fit.

The accurate microwave structure of vinylene carbonate<sup>15</sup> has been used for calculations. It was expected that the involved force constants of 1,3 dioxole-2-one ring would be similar to 1,3 dioxole-2-thione ring.<sup>1</sup> Thus the input for the final calculations of this programme was geometric model, inertial defect,<sup>15</sup> fundamental

vibrational frequencies,<sup>4,5</sup> and force constants similar to 1,3 dioxole-2-thione.<sup>1</sup>

The final results of the least squares procedure together with observed values of the normal vibrations are shown in table 1. Also included in this table is an approximate description of the distribution of potential energy within the various normal modes, as a result of force field used. The final values of the force constants are tabulated in table 2. A comparison of the observed and calculated absorption frequencies (table 1) suggests that the chosen force field is reasonable.

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