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Tentatively Standardized Symmetry Coordinates for Vibrations of Polyatomic Molecules

XII. Some Planar Five-Membered Ring Structures

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Considerable interest is attached to heterocyclic five-membered ring structures, for which some modern spectroscopic and structural investigations have been completed, and further developments are in progress. In the present communication we wish to propose symmetry coordinates of molecular vibrations applicable to the four structures shown in Fig. 1. They are the (i) five-particle ring, which is the skeleton of all the here considered models, (ii) 1,3,4-thiadiazole,^{1,2} (iii) 1,2,5-thiadiazole,³ and (iv) thiophene⁴ or furan⁵ type molecular models.

The considered models all have the symmetry of C_{2v} . Fig. 1 shows the proposed numbering of atoms, which preserves consecutive numbering within each group of symmetrically equivalent atoms.

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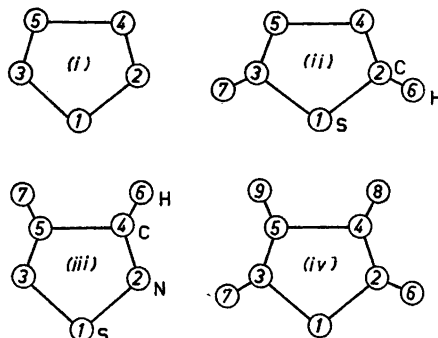


Fig. 1. Five-membered ring structures of C_{2v} symmetry.

It is not difficult to set up a complete set of symmetry coordinates without redundants in several different ways. We have chosen the alternative based on the valence coordinates explained on Fig. 2. Here the parenthesized symbols refer to out-of-plane coordinates: τ is used to denote ring torsions, while γ and ε denote out-of-plane bendings which involve the outer atoms.

Table 1 shows the actual symmetry coordinates. They are applicable to all the models (i, ii, iii, iv) shown in Fig. 1, when the appropriate expressions are selected according to the indication in Table 1.

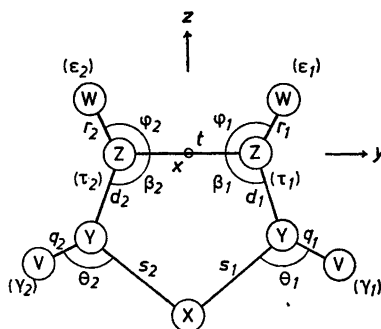


Fig. 2. The planar five-membered ring model $X(YV)_2(ZW)_2$; symmetry C_{2v} . Equilibrium parameters may conveniently be identified by corresponding capital letters. A sufficient set of equilibrium parameters is: $S, D, T, B, Q, \Theta, R, \Phi$.

Table 1. Symmetry coordinates for some planar five-membered ring structures.

Species	Coordinate	(Models)
A_1	$2^{-1/2}(s_1+s_2)$	(i, ii, iii, iv)
	$2^{-1/2}(d_1+d_2)$	(i, ii, iii, iv)
	t	(i, ii, iii, iv)
	$(DT/2)^{1/2}(\beta_1+\beta_2)$	(i, ii, iii, iv)
	$2^{-1/2}(q_1+q_2)$	(ii, iv)
	$2^{-1/2}(r_1+r_2)$	(iii, iv)
	$(QS/2)^{1/2}(\theta_1+\theta_2)$	(ii, iv)
	$(RT/2)^{1/2}(\varphi_1+\varphi_2)$	(iii, iv)
A_2	$(ST/2)^{1/2}(\tau_1+\tau_2)$	(i, ii, iii, iv)
	$[(DS)^{1/2}Q/2]^{1/2}(\gamma_1-\gamma_2)$	(ii, iv)
	$[(DT)^{1/2}R/2]^{1/2}(\varepsilon_1-\varepsilon_2)$	(iii, iv)
B_1	$(ST/2)^{1/2}(\tau_1-\tau_2)$	(i, ii, iii, iv)
	$[(DS)^{1/2}Q/2]^{1/2}(\gamma_1+\gamma_2)$	(ii, iv)
	$[(DT)^{1/2}R/2]^{1/2}(\varepsilon_1+\varepsilon_2)$	(iii, iv)
B_2	$2^{-1/2}(s_1-s_2)$	(i, ii, iii, iv)
	$2^{-1/2}(d_1-d_2)$	(i, ii, iii, iv)
	$(DT/2)^{1/2}(\beta_1-\beta_2)$	(i, ii, iii, iv)
	$2^{-1/2}(q_1-q_2)$	(ii, iv)
	$2^{-1/2}(r_1-r_2)$	(iii, iv)
	$(QS/2)^{1/2}(\theta_1-\theta_2)$	(ii, iv)
	$(RT/2)^{1/2}(\varphi_1-\varphi_2)$	(iii, iv)

It is intended to use the present symmetry coordinates in a spectroscopic analysis of 1,3,4-thiadiazole to be performed in connection with a gas electron-diffraction investigation of this molecule.

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The Influence of Methyl Groups on Electron Distribution and Photocycloaddition Reactions of α,β -Unsaturated Carbonyl Compounds

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Although the photocycloaddition of α,β -unsaturated carbonyl compounds to olefins and related reactions have been extensively studied in recent years,¹ some aspects of the mechanism remain obscure. One interesting problem is the nature of the attack of the excited carbonyl compound on the olefin.

The carbonyl compound, generally in the $n \rightarrow \pi^*$ excited state,¹ could behave either as an electrophile or as a diradical. When several isomeric addition products are possible, their relative yields should be determined, in an electrophilic type of reaction by the charge distribution but in a radical type of reaction by the unpaired electron density in the highest occupied

Table 1. Relative charge in the first $n \rightarrow \pi^*$ excited state of acrolein and its 2- and 3-methyl derivatives.

	h_{O}	Charge on atom			
		O ^a	C ₁	C ₂	C ₃
Acrolein	1	0.54	0.25	0.16	0.05
	2.5	0.35	0.31	0.20	0.15
2-Methyl acrolein "inductive model"	1	0.53	0.17	0.36	-0.06
	2.5	0.34	0.23	0.38	0.05
"hetero atom model"	1	0.68	0.37	0.35	0.15
	2.5	0.50	0.43	0.38	0.26
3-Methylacrolein "inductive model"	1	0.48	0.15	0.07	0.30
	2.5	0.33	0.18	0.10	0.38
"hetero atom model"	1	0.66	0.37	0.27	0.25
	2.5	0.49	0.40	0.31	0.34

^a Corrected with +1 corresponding to loss of the n -electron.