UREY-BRADLEY FORCE FIELD—ALLENE (C_3H_4)

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The Urey-Bradley force field has been employed in the investigation of force constants for the allene molecule. Using the Urey-Bradley force constants, the vibrational wavenumbers have been calculated and compared with the observed bands reported for this molecule.

Introduction

The infra-red and Raman spectra of allene have been studied experimentally by several authors.[1–6] The nondegenerate normal modes of vibration have been investigated by Thompson and Linnett[7] and by Ta-You-Wu.[8] Herzberg[9] has discussed the symmetry properties of the vibration and the assignments of the observed bands. The normal vibrations of the molecule have been studied by Venkateswarlu and Krishna Pillai[10] using the Wilson F-G matrix method. In the present investigation, the Urey-Bradley force field has been applied to the evaluation of force constants of this molecule.

Symmetry, F-Matrix and G-Matrix

The allene molecule has the symmetry D_{2d} (V_d). According to the well-known selection rules, there are $3a_1 + 1b_1 + 3b_2 + 4e$ types of vibration. The symmetry co-ordinates used in this investigation are those given by Herman and Shaffer.[11] b_1 represents the out of plane vibration and was not considered here.

The elements of the F matrix obtained using the Urey-Bradley type of potential function are given below for the different vibrational species:

For the a_1 type:

$$F_{11} = K_r + 2S^2 F_{HH} + t_1^2 F'_{CH} + S_1^2 F_{CH}$$

$$F_{22} = K_R + 4 (t_0^2 F'_{CH} + S_0^2 F_{CH})$$

$$F_{33} = r_0^2 (H_{HH} - S^2 F'_{HH} + t^2 F_{HH})$$

$$F_{12} = \sqrt{2} (- t_0 t_1 F'_{CH} + S_0 S_1 F_{CH})$$

$$F_{13} = \sqrt{2}\,\rho_1\,(R_0 r_0)^{1/2}\,(t_0 S_1 F'_{CH} + S_0 t_1 F_{CH})$$

$$F_{23} = 0$$

For the b_2 type:

$$F_{77} = K_r + 2S^2F_{HH} + t_1^2F'_{CH} + S_1^2F_{CH}$$

$$F_{88} = K_R + 4\,(t_0^2F'_{CH} + S_0^2F_{CH})$$

$$F_{99} = r_0^2\,(H_{HH} - S^2F'_{HH} + t^2F_{HH})$$

$$F_{78} = -\sqrt{2}\,(-t_0t_1F'_{CH} + S_0S_1F_{CH})$$

$$F_{79} = -\sqrt{2}\,\rho_1\,(R_0r_0)^{1/2}\,(t_0S_1F'_{CH} + S_0t_1F_{CH})$$

$$F_{89} = 0$$

and for the e type:

$$F_{10\,10} = K_r + 2t^2F'_{HH} + t_1^2F'_{CH} + S_1^2F_{CH}$$

$$F_{11\,11} = R_0^2H_{CC}$$

$$F_{12\,12} = r_0^2\cos^2\alpha/2H_\eta$$

$$F_{13\,13} = R_0r_0\,(R_{CH} - S_0S_1F'_{CH} + t_0t_1'F_{CH})$$

$$F_{10\,13} = \rho_0\,(R_0r_0)^{1/2}\,(t_1S_0F'_{CH} + S_1t_0F_{CH}),$$

and all the other elements are zero,

where K_R and K_r are the stretching force constants, H_{HH}, H_{CH}, H_{CC} and H_η are the bending force constants,[10] F_{HH} and F_{CH} are the repulsion force constants ($F'_{HH} = -F_{HH}/10$ and $F'_{CH} = -F_{CH}/10$). The S's, t's and ρ's have the usual significance.

The elements of the G-matrix obtained by Venkateswarlu and Krishna Pillai[10] were made use of in these calculations.

The molecular parameters[12] used in this investigation are:

r (C—H) = 1·06 Å R (C—C) = 1·34 Å

α (H—C—H) = 109° 28′ β (H—C—C) = 125° 16′.

The force constants and repulsion constants for allene are listed in Table I along with the results obtained by Venkateswarlu and Krishna Pillai.[10] The calculated wavenumbers are also given in Table I together with the observed wavenumbers for comparison.

TABLE I

Force constants (10^5 *dynes/cm.*) *and calculated and observed wavenumbers*[13] ($cm.^{-1}$)

Force constant	Present values U.B.F.F.	Venkateswarlu and Krishna Pillai F-G matrix*	Species	Wave numbers	
				Observed	Calculated
K_{CC}	9·372	9·947	a_1	1071	1071
K_{CH}	4·629	5·063		2993	2993
H_{HH}	0·464	0·5896		1430	1426
H_{CH}	0·243	0·3000	e	353	353
H_{CC}	0·198	0·1593		1030	1033
H_{η}	1·649	1·0710		3061	3052
F_{HH}	0·057	..		850	850
F_{CH}	0·381	..	b_2	1960	1986
				2960	2951
				1390	1390

* The interaction constants are not entered in the table.

It can be seen from Table I that the values of force constants obtained in this investigation compare well with those of Venkateswarlu and Krishna Pillai.[10] Also, the wavenumbers calculated using the U.B. force constants are in good agreement with the observed fundamentals.

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