Theoret. Chim. Acta (Berl.) 49, 1–11 (1978)

THEORETICA CHIMICA ACTA

Original Investigations

Simple Electrostatic Models for Vibrating Unsymmetrical Triatomic Molecules and Triatomic Ions*

José Luis Gázquez**
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, USA

N. K. Ray*** and Robert G. Parr
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, USA

Bond charge, point-dipole models are used to derive simple universal relations, $K_{\theta\theta}=0.0435\ (\mathrm{K}_{11}K_{22})^{1/2}-0.0086\ (K_{11}^{+}K_{22})$, and $K_{\theta\theta}=0.11\ (K_{11}K_{22})^{1/2}-0.0055\ (K_{11}+K_{22})$, between the bond stretching force constants K_{11} and K_{22} and bond bending force constant $K_{\theta\theta}$ for linear and bent unsymmetrical triatomic molecules respectively. The relations are shown to be approximately valid for a number of molecules. An extension of the models to include charged species (ions) in triatomic molecules is also presented and tested, giving good results.

Key words: Bond charge model – Unsymmetric triatomic molecules

1. Introduction

Recently the simple bond-charge (SBC) model has been used [1–9] successfully to predict values for force constants in diatomic, triatomic and polyatomic molecules. In the present work we describe the use of the SBC model to predict various force constants of linear and bent unsymmetrical triatomic molecules, and linear and bent triatomic ions.

The vibrational problem of a triatomic system is most often described in terms of a quadratic valence force field [10]. The force field is given in terms of the bond

---

* Based on part of a thesis submitted by José L. Gázquez in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University, 1976, and aided by research grants to the Johns Hopkins University and University of North Carolina from the National Institutes of Health and the National Science Foundation.

** Present address: Facultad de Química, Universidad Nacional Autónoma de México, México 20, D.F.

*** Present address: Department of Chemistry, University of Delhi, Delhi-7, India.

0040–5744/78/0049/0001/$02.20

stretching force constants K_{11} and K_{22}, the bond–bond interaction constants K_{12}, $K_{1\theta}$, $K_{2\theta}$ and the bending force constants $K_{\theta\theta}$. Following Simons [6] K_{11}, K_{22}, K_{12}, $K_{1\theta}$, $K_{2\theta}$ and $K_{\theta\theta}$ can be expressed as follows:

$$R_{1\mathrm{e}}K_{11}+R_{2\mathrm{e}}K_{12}=\left(\frac{\partial V}{\partial R_1}\right)_{\mathrm{eq.}}, \tag{1}$$

$$R_{2\mathrm{e}}K_{22}+R_{1\mathrm{e}}K_{12}=\left(\frac{\partial V}{\partial R_2}\right)_{\mathrm{eq.}}, \tag{2}$$

$$R_{1\mathrm{e}}^2K_{1\theta}+R_{2\mathrm{e}}^2K_{2\theta}=\left(\frac{\partial V}{\partial \theta}\right)_{\mathrm{eq.}}, \tag{3}$$

and

$$K_{\theta\theta}\simeq\frac{1}{2R_{1\mathrm{e}}R_{2\mathrm{e}}}\left(\frac{\partial^2 V}{\partial \theta^2}\right)_{\mathrm{eq.}}. \tag{4}$$

Here $V\equiv V(R_1, R_2, \theta)$ is the electronic potential energy as a function of configuration; $R_{1\mathrm{e}}$ is the equilibrium XY distance and $R_{2\mathrm{e}}$ is the equilibrium YZ distance.

To get an estimate of the force constants on the left side of Eqs. [1–4] only V needs to be explicitly modeled.

2. Model for Unsymmetric Triatomic Molecules

The potential energy is modelled as follows: 1) Place a charge $-q_{\mathrm{xy}}\mathrm{e}$ at the center of the XY bond. 2) Place a charge $-q_{\mathrm{yz}}\mathrm{e}$ at the center of the YZ bond. 3) Place a charge $(q_{\mathrm{xy}}+q_{\mathrm{yz}})\mathrm{e}/3$ on each nucleus 4) Place a point dipole on the central nucleus (to produce non-linear equilibrium geometries). The potential energy V then takes the explicit form:

$$\begin{aligned}V=&-\frac{11}{9}\frac{q_{\mathrm{xy}}^2\mathrm{e}^2}{R_1}-\frac{10}{9}\frac{q_{\mathrm{xy}}q_{\mathrm{yz}}\mathrm{e}^2}{R_1}+\frac{1}{9}\frac{q_{\mathrm{yz}}^2\mathrm{e}^2}{R_1}-\frac{11}{9}\frac{q_{\mathrm{yz}}^2\mathrm{e}^2}{R_2}-\frac{10}{9}\frac{q_{\mathrm{xy}}q_{\mathrm{yz}}\mathrm{e}^2}{R_2}\\&+\frac{1}{9}\frac{q_{\mathrm{xy}}^2\mathrm{e}^2}{R_2}+\frac{[2q_{\mathrm{xy}}q_{\mathrm{yz}}+(1/9)(q_{\mathrm{xy}}+q_{\mathrm{yz}})^2]\mathrm{e}^2}{(R_1^2+R_2^2-2R_1R_2\cos\theta)^{1/2}}\\&-\frac{q_{\mathrm{xy}}(q_{\mathrm{xy}}+q_{\mathrm{yz}})\mathrm{e}^2}{3(\frac{1}{4}R_1^2+R_2^2-R_1R_2\cos\theta)^{1/2}}-\frac{q_{\mathrm{yz}}(q_{\mathrm{xy}}+q_{\mathrm{yz}})\mathrm{e}^2}{3(R_1^2+\frac{1}{4}R_2^2-R_1R_2\cos\theta)^{1/2}}\\&-\frac{11}{3}\frac{q_{\mathrm{xy}}\mathrm{e}\mu\cos\frac{1}{2}\theta}{R_1^2}+\frac{1}{3}\frac{q_{\mathrm{yz}}\mathrm{e}\mu\cos\frac{1}{2}\theta}{R_1^2}\\&-\frac{11}{3}\frac{q_{\mathrm{yz}}\mathrm{e}\mu\cos\frac{1}{2}\theta}{R_2^2}+\frac{1}{3}\frac{q_{\mathrm{xy}}\mathrm{e}\mu\cos\frac{1}{2}\theta}{R_2^2}\end{aligned} \tag{5}$$

Substituting this expression for V into Eqs. (1), (2) and (3), gives q_{xy}, q_{yz} and μ in terms of $R_{1\mathrm{e}}$, $R_{2\mathrm{e}}$, K_{11}, K_{22}, K_{12}, $K_{1\theta}$ and $K_{2\theta}$ (see Appendix). Then the bending force constant $K_{\theta\theta}$ may be determined from these values, using Eq. (4).

Table 1. Parameters for the model, and predicted bending force constants[a]

Molecule	q_{xy}	q_{yz}	μ	$K_{\theta\theta}$ (Calc.)	$K_{\theta\theta}$ (Exptl.)[c]
OCS	1.97	2.41	0.0	0.22	0.37
OCSe	2.03	2.27	0.0	0.181	0.29
SCSe	2.27	2.27	0.0	0.146	0.20
SCTe	1.72	2.81	0.0	0.099	0.175
HCN	0.74	2.88	0.0	0.044	0.212
N_2O	2.67	1.46	0.0	0.272	0.508
ClCN	2.04	2.05	0.0	0.182	0.212
BrCN	1.87	2.14	0.0	0.153	0.183
ICN	1.77	2.18	0.0	0.124	0.135
ONF[b]	2.42	0.76	2.38	0.321	1.00
	(2.44)	(1.18)	(2.74)	(0.555)	
ONCl[b]	2.32	0.96	2.56	0.197	0.60
	(2.36)	(1.38)	(2.93)	(0.289)	
ONBr[b]	2.32	1.06	2.63	0.180	0.46
	(2.34)	(1.60)	(3.09)	(0.262)	

[a] Values calculated using Eqs. (A1–A4) of the Appendix. q_{xy} and q_{yz} in atomic units, μ in debyes and $K_{\theta\theta}$ in millidynes/Å.

[b] Values in parentheses obtained including K_{12}.

[c] Experimental data from Refs. [11–17].

The q_{xy}, q_{yz} and μ values for several triatomic molecules are given in Table 1. These calculations were done assuming $K_{1\theta}\approx 0$, $K_{2\theta}\approx 0$ for bent molecules; for linear molecules they are exactly equal to zero. K_{12} was neglected in Eqs. (1) and (2) since it is generally much smaller than K_{11} and K_{22}. As in all previous calculations, the resultant q values appear to be reasonable measures of bond order.

The values of $K_{\theta\theta}$ predicted are also given in Table 1. The agreement with experimental values is reasonable and the trend within a group is correct. The values of ONF, ONCl and ONBr are somewhat low. As these molecules have large K_{12} values, of the same magnitude as K_{22}, a large error is introduced by the approximations we have made. The values obtained when K_{12} is included are presented, in parentheses, in Table 1.

3. The Approximations to the Model

The parameters q_{xy}, q_{yz} and μ, that were determined through the potential energy given by Eq. (5) and Eqs. (1–3), may be estimated from other sources.

3.1. *Linear XYX, ZYZ in Linear XYZ*

If q_{xy} and q_{yz} are estimated from the corresponding symmetric triatomic molecules XYX and ZYZ, Eqs. (1) and (2) give the formulas [7]

$$K_{11}+K_{12}=\frac{37}{18}\frac{q_{xy}^2 e^2}{R_{1e}^3}, \tag{6}$$

$$K_{22}+K_{12}=\frac{37}{18}\frac{q_{yz}^2 e^2}{R_{2e}^3}. \tag{7}$$

It should be pointed out that although these relations correspond to the symmetric case, one uses the experimental values K_{11}, K_{22}, K_{12}, R_{1e} and R_{2e} of the XYZ molecule to estimate the bond charges, thus $K_{\theta\theta}$ can be predicted from Eq. (5) setting $\mu=0$. However, one may further assume that $R_{1e}\approx R_{2e}$, leading to a universal relationship between K_{11}, K_{22}, K_{12} and $K_{\theta\theta}$; namely,

$$K_{\theta\theta}=0.0435[(K_{11}+K_{12})(K_{22}+K_{12})]^{1/2}-0.0086(K_{11}+K_{22}+2K_{12}). \tag{8}$$

If K_{12} is neglected, this reduces to

$$K_{\theta\theta}=0.0435(K_{11}K_{22})^{1/2}-0.0086(K_{11}+K_{22}). \tag{9}$$

For XY_2 molecules, $K_{11}=K_{22}$, and Eq. (9) reduces to the relation derived in Ref. [7].

The form of Eq. (9) suggests other possible formulas, like

$$K_{\theta\theta}=0.026(K_{11}K_{22})^{1/2}, \tag{10}$$

or

$$K_{\theta\theta}=0.026[\tfrac{1}{2}(K_{11}+K_{22})] \tag{11}$$

These formulas result from taking the geometrical mean or the arithmetical mean of K_{11} and K_{22} in the unsymmetrical molecule, and using the proportionality constant of the symmetrical case [7].

The values of $K_{\theta\theta}$ predicted from Eqs. (9–11) are given in Table 2. The agreement with experimental values is quite good. Eq. (9) gives the best results. Calculations without assuming $R_{1e}\approx R_{2e}$, are also reported in Table 2 in parentheses. It may be seen from these results that the effect of assuming $R_{1e}\approx R_{2e}$ is small.

3.2. *Bent XYX and ZYZ in Bent XYZ*

As in the foregoing, one uses the values of K_{11} and K_{22} of the unsymmetrical molecule in the expressions obtained for the symmetrical case to determine q_{xy}, q_{yz} and μ; then $K_{\theta\theta}$ may be evaluated. However, rather than calculating each molecule in particular, we can proceed following Simons and Choc [8] to find a universal relationship between $K_{\theta\theta}$, K_{11} and K_{22}. Thus again making the approximation $R_{1e}\approx R_{2e}$, one obtains

$$K_{\theta\theta}=G_1(\theta e)[(K_{11}+K_{12})(K_{22}+K_{12})]^{1/2}+G_2(\theta e)[K_{11}+K_{22}+2K_{12}]. \tag{12}$$

$G_1(\theta e)$ and $G_2(\theta e)$ are functions of the equilibrium angle defined in the Appendix. It is found that for angles between 90° and 135°, which include most triatomic

Table 2. Predicted bending force constants from different relationships for linear XYZ molecules[a]

Molecule	$K_{\theta\theta}$ (Calc.)[b, c]				$K_{\theta\theta}$ (Exptl.)
	Eq. (9)		Eq. (10)	Eq. (11)	
OCS	0.283	(0.273)	0.292	0.311	0.37
OCSe	0.240	(0.229)	0.257	0.290	0.29
SCSe	0.181	(0.181)	0.180	0.180	0.20
SCTe	0.150	(0.138)	0.148	0.148	0.175
HCN	0.255	(0.232)	0.281	0.325	0.212
N_2O	0.382	(0.374)	0.384	0.394	0.508
ClCN	0.215	(0.219)	0.240	0.283	0.212
BrCN	0.184	(0.191)	0.218	0.273	0.183
ICN	0.136	(0.151)	0.182	0.255	0.135
LiCN	0.030		0.119	0.254	0.045
LiNC	0.055		0.123	0.229	0.017
CsOH	0.046		0.071	0.111	0.020
RbOH	0.049		0.073	0.111	0.021
NaOH	0.050		0.074	0.111	0.028

[a] See text.

[b] $K_{\theta\theta}$ in millidynes/Å. Experimental values from Refs. [11–14].

[c] Values in parentheses obtained using the expressions for symmetric molecules to determine the parameters q_{xy}, q_{yz} and μ, but without assuming $R_{1e} \approx R_{2e}$ in the expression for $K_{\theta\theta}$ (Eq. (A4) of Appendix).

molecules, $G_1(\theta e)$ and $G_2(\theta e)$ are slowly varying functions with average values of $G_1(\theta e) = 0.1100$ and $G_2(\theta e) = -0.0055$, therefore Eq. (12) can be written as

$$K_{\theta\theta} = 0.1100[(K_{11}+K_{12})(K_{22}+K_{12})]^{1/2} - 0.0055[K_{11}+K_{22}+2K_{12}] \qquad (13)$$

or, if K_{12} is neglected,

$$K_{\theta\theta} = 0.1100(K_{11}K_{22})^{1/2} - 0.0055(K_{11}+K_{22}). \qquad (14)$$

Eq. (14) reduces to the relation derived in Ref. [8] when $K_{11} = K_{22}$. Values of $K_{\theta\theta}$ predicted using Eq. (14) are given in Table 3.

Table 3. Predicted bending force constants from Eq. (14) for bent XYZ molecules[a]

Molecule	$K_{\theta\theta}$(Calc.) Eq. (14)		$K_{\theta\theta}$[b] (Exptl.)
ONF	0.563	(0.877)	1.00
ONCl	0.402	(0.649)	0.60
ONBr	0.374	(0.628)	0.46
LiON	0.3116		0.255
FCO	0.753		0.940
ClCO	0.435		0.240

[a] See text. Values in parentheses calculated with Eq. (13) of the text.

[b] $K_{\theta\theta}$ in millidynes/Å. Experimental values from Refs. [15–17].

3.3. *Diatomics XY and YZ in Triatomic XYZ*

This model uses values of q_{xy} and q_{yz} appropriate for the diatomic molecules XY and YZ. Thus K_{11}, and K_{22} and $K_{\theta\theta}$ may be predicted. The expressions for q_{xy} and q_{yz} are [2]:

$$q_{xy}=\frac{4}{7}\left(\frac{k_{xy}R_{xy}^3}{e^2}\right)^{1/2}, \tag{15}$$

$$q_{yz}=\frac{4}{7}\left(\frac{k_{yz}R_{yz}^3}{e^2}\right)^{1/2}, \tag{16}$$

where k_{xy}, R_{xy} and k_{yz}, R_{yz} are the force constants and equilibrium distances of the diatomic molecules XY and YZ. Results using this approximation are given in Table 4. The values of K_{11} and K_{22} are overestimated in general; however, a good estimate of $K_{\theta\theta}$ is obtained.

Table 4. Predicted stretching force constants and bending force constants using diatomic bond charges[a, b]

Molecule	Diatomic q_{xy}	q_{yz}	K_{11} (Calc.)	K_{11} (Exptl.)	K_{22} (Calc.)	K_{22} (Exptl.)	$K_{\theta\theta}$ (Calc.)	$K_{\theta\theta}$ (Exptl.)
OCS	2.60	2.75	25.8	16.02	11.0	7.86	0.343	0.37
OCSe	2.60	2.76	25.6	16.02	9.25	6.1	0.285	0.29
SCSe	2.75	2.76	11.6	7.86	8.98	6.1	0.216	0.20
SCTe	2.75	3.49	13.1	5.90	9.40	5.46	0.219	0.175
HCN	1.25	2.55	11.0	6.23	17.5	18.77	0.232	0.212
N_2O	2.75	2.45	24.1	18.48	24.8	11.83	0.539	0.508
ClCN	2.27	2.55	6.77	5.15	24.3	16.6	0.255	0.212
BrCN	1.90	2.55	4.74	4.17	22.3	16.8	0.188	0.183
ICN	1.56	2.55	2.73	2.94	20.3	16.7	0.128	0.135

[a] q_{xy} and q_{yz} from Eqs. (15) and (16). K_{11}, K_{22} and $K_{\theta\theta}$ from Eqs. (A1), (A2) and (A4).

[b] q_{xy} and q_{yz} in atomic units. K_{11}, K_{22} and $K_{\theta\theta}$ in millidynes/Å.

4. Model for Linear Symmetric Triatomic Ions

For charged species $(XY_2)^n$, V is modelled by placing charges $+(2q+n)e/3$ at each atom and $-q_e$ at the middle of each bond, where n is the charge of the ion. The potential energy is then given by the formula,

$$\begin{aligned} V= & -\frac{(20q^2+8qn-n^2)e^2}{9R_1}-\frac{(20q^2+8qn-n^2)e^2}{9R_2} \\ & +\frac{(22q^2+4qn+n^2)e^2}{9(R_1^2+R_2^2-2R_1R_2\cos\theta)^{1/2}}-\frac{(2q^2+qn)e^2}{3(R_1^2+R_2^2/4-R_1R_2\cos\theta)^{1/2}} \\ & -\frac{(2q^2+qn)e^2}{3(R_1^2/4+R_2^2-R_1R_2\cos\theta)^{1/2}} \end{aligned} \tag{17}$$

where R_1 and R_2 are the X–Y and Y–X distances and θ is the YXY angle.

Using this expression for V in Eqs. (1) and (4), we get the following expressions for a linear symmetric ion of the type $(XY_2)^n$:

$$K_{11}+K_{12}=\frac{(74q^2+36qn-5n^2)e^2}{36R_e^3}, \tag{18}$$

$$K_{\theta\theta}=\frac{(70q^2-28qn+9n^2)e^2}{1296R_e^3}. \tag{19}$$

If the molecule is neutral ($n=0$), Eqs. (18) and (19) reduce to the results obtained earlier [7]. Eq. (18) has been used to estimate the triatomic bond charges (q values) for ions; results are given in Table 5 along with the corresponding diatomic values. It can be seen that the two sets of values are similar. This is consistent with the notion of localized and relatively independent chemical bonds.

Table 5. Comparison of diatomic and triatomic q values, and predicted bending force constants[a]

			$K_{11}+K_{12}$		$K_{\theta\theta}$		
Molecule	q (diatomic)	q (triatomic)	I	Exptl.	I	II	Exptl.
I_3^-	2.83	2.52	1.24	0.95	0.05	0.04	0.03
IBr_2^-	2.78	2.54	1.57	1.28	0.06	0.05	0.04
ICl_2^-	2.72	2.49	1.79	1.47	0.07	0.06	0.10
Br_3^-	2.68	2.42	1.68	1.33	0.06	0.05	0.02
$BrCl_2^-$	2.54	2.40	1.83	1.61	0.07	0.06	0.11
HF_2^-	1.36	1.36	3.71	4.03	0.22	0.23	0.22
HCl_2^-	1.63	1.38	2.19	1.41	0.11	0.08	0.06
HBr_2^-	1.70	1.52	2.01	1.37	0.09	0.07	0.04
N_3^-	2.73	2.54	17.48	14.90	0.66	0.58	0.58
NO_2^+	2.46	2.22	22.18	18.36	0.42	0.34	0.47
ICl_2^+[b]	2.72	1.50	4.30	2.19	0.58	0.18	0.19
BrF_2^+[b]	2.33	1.41	7.63	4.60	0.98	0.36	0.47
ClF_2^+[b]	2.21	1.32	8.36	4.74	0.98	0.38	0.60
NSC^-[c]	2.55(2.75)	2.42(2.30)	16.17(14.35)	8.02 (5.34)	0.41	0.335	0.203
NSO^-[c]	2.55(2.60)	2.51(2.37)	15.36(14.84)	13.82(11.17)	0.56	0.508	0.501

[a] Triatomic q values obtained using Eq. (18) of text. Diatomic q values obtained from Eq. (15) of text. Experimental data from Refs. [18–26]. $K_{\theta\theta}$ in millidynes/Å. Numbers given under *I* obtained using diatomic bond charges. $K_{\theta\theta}$ values given under *II* obtained using triatomic bond charges.

[b] Bent molecules. K_{12} neglected in these cases.

[c] Values in parentheses correspond to the YZ bond. Experimental values from Refs. [11]. K_{12} neglected.

The triatomic bond charges are used in Eq. (19) to estimate $K_{\theta\theta}$ values for the triatomic ions; results are given under column 2 in Table 5. There is good agreement with experimental results.

Estimation of $K_{11}+K_{12}$ and $K_{\theta\theta}$ can also be made from Eqs. (18) and (19) by assuming diatomic and triatomic bond charges (q) to be equal. Estimates of $K_{11}+K_{12}$ and $K_{\theta\theta}$ obtained using diatomic bond charges are given under column 1 in Table 5. The predicted results again are in reasonable agreement with experimental values.

5. Other Triatomic Species and Conclusions

For bent symmetrical ions, one just has to place a point dipole on central atoms; results for three such species are reported in Table 5.

The extension of these models to include unsymmetrical ions is straightforward following the models derived in Sects. 2 and 4. Some results are also presented in Table 5.

It may be concluded from the results obtained here and the earlier work, that the SBC models are very useful to establish a semiempirical scheme for the estimation of the bending force constants, providing simple relations which are justified through a physical model. The bending and stretching force constants can be semiquantitatively accounted for using a single electrostatic model with reasonable values for the parameters.

Appendix

The quantities q_{xy}, q_{yz}, μ and $K_{\theta\theta}$ may be determined in the manner suggested in Sect. 1. The equations that result from substituting the potential energy V, Eq. (5) into Eqs. (1–4), and evaluating these expressions at equilibrium are as follows:

$$\begin{aligned}R_{1e}K_{11}+R_{2e}K_{12}= & \\ & \frac{11}{9}\frac{q_{xy}^2 e^2}{R_{1e}^2}+\frac{10}{9}\frac{q_{xy}q_{yz}e^2}{R_{1e}^2}-\frac{1}{9}\frac{q_{yz}^2 e^2}{R_{1e}^2} \\ & +\frac{q_{xy}(q_{xy}+q_{yz})e^2}{6}\frac{\frac{1}{2}R_{1e}-R_{2e}\cos\theta e}{(\frac{1}{4}R_{1e}^2+R_{2e}^2-R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & +\frac{q_{yz}(q_{xy}+q_{yz})e^2}{3}\frac{R_{1e}-\frac{1}{2}R_{2e}\cos\theta e}{(R_{1e}^2+\frac{1}{4}R_{2e}^2-R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & -\frac{[2q_{xy}q_{yz}e^2(R_{1e}-R_{2e}\cos\theta e)+\frac{1}{9}(q_{xy}+q_{yz})^2e^2(R_{1e}-R_{2e}\cos\theta e)]}{(R_{1e}^2+R_{2e}^2-2R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & +\frac{22}{3}\frac{q_{xy}e\mu\cos\frac{1}{2}\theta e}{R_{1e}^3}-\frac{2}{3}\frac{q_{yz}e\mu\cos\frac{1}{2}\theta e}{R_{1e}^3},\end{aligned}\tag{A1}$$

$$\begin{aligned}R_{2e}K_{22}+R_{1e}K_{12}= & \frac{11}{9}\frac{q_{yz}^2 e^2}{R_{2e}^2}+\frac{10}{9}\frac{q_{xy}q_{yz}e^2}{R_{2e}^2}-\frac{1}{9}\frac{q_{xy}^2 e^2}{R_{2e}^2} \\ & +\frac{q_{yz}(q_{xy}+q_{yz})e^2}{6}\frac{\frac{1}{2}R_{2e}-R_{1e}\cos\theta e}{(R_{1e}^2+\frac{1}{4}R_{2e}^2-R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & +\frac{q_{xy}(q_{xy}+q_{yz})e^2}{3}\frac{R_{2e}-\frac{1}{2}R_{1e}\cos\theta e}{(\frac{1}{4}R_{1e}^2+R_{2e}^2-R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & -\frac{[2q_{xy}q_{yz}e^2+\frac{1}{9}(q_{xy}+q_{yz})^2e^2](R_{2e}-R_{1e}\cos\theta e)}{(R_{1e}^2+R_{2e}^2-2R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & +\frac{22}{3}\frac{q_{xy}\,e\mu\cos\frac{1}{2}\theta e}{R_{2e}^3}-\frac{2}{3}\frac{q_{xy}e\mu\cos\frac{1}{2}\theta e}{R_{2e}^3},\end{aligned}\tag{A2}$$

$$\begin{aligned} R_{1e}^2 K_{1\theta} + R_{2e}^2 K_{2\theta} = & -\frac{[2q_{xy}q_{yz}e^2 + \frac{1}{9}(q_{xy}+q_{yz})^2 e^2] R_{1e} R_{2e} \sin\theta e}{(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & + \frac{q_{xy}(q_{xy}+q_{yz})e^2}{6} \frac{R_{1e}R_{2e}\sin\theta e}{(\frac{1}{4}R_{1e}^2 + R_{2e}^2 - R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & + \frac{q_{yz}(q_{xy}+q_{yz})e^2}{6} \frac{R_{1e}R_{2e}\sin\theta e}{(R_{1e}^2 + \frac{1}{4}R_{2e}^2 - R_{1e}R_{2e}\cos\theta e)^{3/2}} \\ & + \frac{11}{6}\frac{q_{xy}e\mu\sin\frac{1}{2}\theta e}{R_{1e}^2} - \frac{1}{6}\frac{q_{yz}e\mu\sin\frac{1}{2}\theta e}{R_{1e}^2} \\ & + \frac{11}{6}\frac{q_{yz}e\mu\sin\frac{1}{2}\theta e}{R_{2e}^2} - \frac{1}{6}\frac{q_{xy}e\mu\sin\frac{1}{2}\theta e}{R_{2e}^2}, \end{aligned} \qquad \text{(A3)}$$

and

$$K_{\theta\theta} = F_1 q_{xy} q_{yz} e^2 + F_2 q_{xy}^2 e^2 + F_3 q_{yz}^2 e^2 + F_4 \mu q_{xy} e + F_5 \mu q_{yz} e, \qquad \text{(A4)}$$

where:

$$\begin{aligned} F_1 = & -\frac{10}{9}\frac{\cos\theta e(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e) - 3\sin^2\theta e R_{1e}R_{2e}}{(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e)^{5/2}} \\ & + \frac{1}{12}\frac{\cos\theta e(\frac{1}{4}R_{1e}^2 + R_{2e}^2 - R_{1e}R_{2e}\cos\theta e) - \frac{3}{2}\sin^2\theta e R_{1e}R_{2e}}{(\frac{1}{4}R_{1e}^2 + R_{2e}^2 - R_{1e}R_{2e}\cos\theta e)^{5/2}} \\ & + \frac{1}{12}\frac{\cos\theta e(R_{1e}^2 + \frac{1}{4}R_{2e}^2 - R_{1e}R_{2e}\cos\theta e) - \frac{3}{2}\sin^2\theta e R_{1e}R_{2e}}{(R_{1e}^2 + \frac{1}{4}R_{2e}^2 - R_{1e}R_{2e}\cos\theta e)^{5/2}} \end{aligned} \qquad \text{(A5)}$$

$$\begin{aligned} F_2 = & \frac{1}{12}\frac{\cos\theta e(\frac{1}{4}R_{1e}^2 + R_{2e}^2 - R_{1e}R_{2e}\cos\theta e) - \frac{3}{2}\sin^2\theta e R_{1e}R_{2e}}{(\frac{1}{4}R_{1e}^2 + R_{2e}^2 - R_{1e}R_{2e}\cos\theta e)^{5/2}} \\ & - \frac{1}{18}\frac{\cos\theta e(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e) - 3\sin^2\theta e R_{1e}R_{2e}}{(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e)^{5/2}}, \end{aligned} \qquad \text{(A6)}$$

$$\begin{aligned} F_3 = & \frac{1}{12}\frac{\cos\theta e(R_{1e}^2 + \frac{1}{4}R_{2e}^2 - R_{1e}R_{2e}\cos\theta e) - \frac{3}{2}\sin^2\theta e R_{1e}R_{2e}}{(R_{1e}^2 + \frac{1}{4}R_{2e}^2 - R_{1e}R_{2e}\cos\theta e)^{5/2}} \\ & - \frac{1}{18}\frac{\cos\theta e(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e) - 3\sin^2\theta e R_{1e}R_{2e}}{(R_{1e}^2 + R_{2e}^2 - 2R_{1e}R_{2e}\cos\theta e)^{5/2}}, \end{aligned} \qquad \text{(A7)}$$

$$F_4 = \frac{11}{24}\frac{\cos\frac{1}{2}\theta e}{R_{1e}^3 R_{2e}} - \frac{1}{24}\frac{\cos\frac{1}{2}\theta e}{R_{2e}^3 R_{1e}}, \qquad \text{(A8)}$$

and

$$F_5 = \frac{11}{24}\frac{\cos\frac{1}{2}\theta e}{R_{2e}^3 R_{1e}} - \frac{1}{24}\frac{\cos\frac{1}{2}\theta e}{R_{1e}^3 R_{2e}}. \qquad \text{(A9)}$$

Thus, knowing K_{11}, K_{22}, R_{1e} and R_{2e}, and neglecting K_{12}, $K_{1\theta}$ and $K_{2\theta}$, the parameters q_{xy}, q_{yz} and μ may be determined from Eqs. (A1–3), and $K_{\theta\theta}$ may be estimated from Eq. (A4).

To derive a universal relationship in bent unsymmetrical triatomic molecules, the approximation $R_{1_e} \approx R_{2_e}$ is made, and the bending force constant is given by

$$K_{\theta\theta} = G_1(\theta e)[(K_{11}+K_{12})(K_{22}+K_{12})]^{1/2} + G_2(\theta e)[(K_{11}+K_{22}+2K_{12}] \quad \text{(A10)}$$

where

$$\begin{aligned} G_1(\theta e) = \frac{H_4}{H_1H_4 - H_2H_3}\Bigg[& \frac{1}{16}\,\frac{\cos\theta e(1-\cos\theta e) - \frac{3}{2}\sin^2\theta e}{(\frac{1}{2})^{5/2}(1-\cos\theta e)^{5/2}} \\ & + \frac{1}{6}\,\frac{\cos\theta e(\frac{5}{4}-\cos\theta e) - \frac{3}{2}\sin^2\theta e}{(\frac{5}{4}-\cos\theta e)^{5/2}} \\ & - \frac{1}{9}\,\frac{2\cos\theta e(1-\cos\theta e) - 3\sin^2\theta e}{2^{5/2}(1-\cos\theta e)^{5/2}}\Bigg], \end{aligned} \quad \text{(A11)}$$

and

$$\begin{aligned} G_2(\theta e) = \frac{H_4}{H_1H_4 - H_2H_3}\Bigg[& \frac{1}{12}\,\frac{\cos\theta e(\frac{5}{4}-\cos\theta e) - \frac{3}{2}\sin^2\theta e}{(\frac{5}{4}-\cos\theta e)^{5/2}} \\ & - \frac{1}{18}\,\frac{2\cos\theta e(1-\cos\theta e) - 3\sin^2\theta e}{2^{5/2}(1-\cos\theta e)^{5/2}} \\ & + \frac{H_3}{H_1H_4 - H_2H_3}\,\frac{5}{12}\cos\frac{1}{2}\theta e\Bigg]\cdot \end{aligned} \quad \text{(A12)}$$

The functions H_1, H_2, H_3 and H_4 are

$$H_1 = \frac{20}{9} - \frac{22}{2^{3/2}(1-\cos\theta e)^{1/2}} + \frac{2}{3(\frac{5}{4}-\cos\theta e)^{1/2}}, \quad \text{(A13)}$$

$$H_2 = -\frac{2^{1/2}.10}{3}(1+\cos\theta e)^{1/2}, \quad \text{(A14)}$$

$$H_3 = -\frac{22}{9}\,\frac{(1+\cos\theta e)^{1/2}}{2^{5/2}(1-\cos\theta e)} + \frac{1}{3}\,\frac{(1-\cos^2\theta e)^{1/2}}{(\frac{5}{4}-\cos\theta e)^{3/2}}, \quad \text{(A15)}$$

and

$$H_4 = -\frac{10}{3.2^{3/2}}(1-\cos\theta e)^{1/2}. \quad \text{(A16)}$$

The functions $G_1(\theta e)$ and $G_2(\theta e)$ were evaluated for angles between 90° and 135°. They were found to be slowly varying functions, with average values of 0.1100 and −0.0055 respectively.

References

1. Parr, R. G., Borkman, R. F.: J. Chem. Phys. **49**, 1055 (1968)
2. Borkman, R. F., Simons, G., Parr, R. G.: J. Chem. Phys. **50**, 58 (1969)
3. Borkman, R. F., Parr, R. G.: J. Chem. Phys. **48**, 1116 (1968)
4. Borkman, R. F.: J Chem. Phys. **51**, 5596 (1969)

5. Borkman, R. F., Settle, Jr., F. A.: J. Am. Chem. Soc. **93**, 5640 (1971)
6. Simons, G.: J. Chem. Phys. **56**, 4310 (1972)
7. Ray, N. K., Parr, R. G.: J. Chem. Phys. **59**, 3934 (1973)
8. Simons, G., Choc, C. E.: Chem. Phys. Letters **25**, 413 (1974)
9. Simons, G., Parr, R. G.: J. Chem. Phys. **55**, 4197 (1971)
10. Herzberg, G.: Molecular spectra and molecular structure, Vols. 1 and 2. Princeton, N.J.: Van Nostrand 1945
11. Jones, L. H.: Inorganic vibrational spectroscopy. New York: Marcel Dekker 1971
12. Wu, T.: Vibrational spectra and structure of polyatomic molecules. Michigan: J. W. Edwards Inc. 1946
13. Ismail, Z. K., Hauge, R. H., Margrave, J. L.: J. Chem. Phys. **57**, 5142 (1972)
14. Acquista, N., Abramowitz, S.: J. Chem. Phys. **51**, 2914 (1969)
15. Andrews, W. L. S., Pimentel, G. C.: J. Chem. Phys. **44**, 2361 (1966)
16. Milligan, D. E : J Chem. Phys. **42**, 3187 (1965)
17. Jacox, M E., Milligan, D. E.: J. Chem. Phys. **43**, 866 (1965)
18. Gabes, W., Elst, R.: J. Mol. Struct. **21**, 1 (1974) and references therein
19. Maki, A. G., Forners, R.: Spectrochim. Acta **23A**, 867 (1967)
20. Nibler, J. W., Pimentel, G.: J. Chem. Phys. **47**, 710 (1967)
21. Evans, J. C., Lo, G. Y.-S : J. Phys. Chem. **70**, 11 (1966)
22. Evans, J. C., Lo, G. Y.-S.: J. Phys. Chem. **71**, 3942 (1967)
23. Siebert, H.: Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie. Berlin: Springer Verlag 1966
24. Ibers, J. A.: J. Chem. Phys. **41**, 25 (1964)
25. Forneris, R., Tavares-Forneris, V.: J. Mol. Struct. **23**, 241 (1974)
26. Gillespie, R. J., Morton, M. J.: Inorg. Chem. **9**, 616 (1970)

Received October 10, 1977