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Calculations on the Force Constants of Triatomic Group II Metal Halides

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A comparison between various polarizable ion models for calculating bending force constants of linear MX_2 molecules is presented. A convergence test is applied to the models. Further, the contribution of an induced dipole-induced quadrupole interaction term to the force constant, is examined. The criteria for a useful comparison between calculated and experimental values of force constants are discussed.

1. Introduction

Several years ago a model was proposed [1] for calculating bending force constants of linear triatomic molecules on the basis of an electrostatic potential. At that time very few experimental results were available. Also numerical errors crept into the calculations. Therefore, it was not possible to test the model, and to compare its results with experiment. In this communication, modified calculations are presented, a comparison is made between different models, and a convergence test is applied. Further, the effect of a new interaction term, namely induced dipole-induced quadrupole is examined.

To avoid being cumbersome, the principles of the method will not be described. Ref. [1] should be consulted for the background of our arguments.

2. Bending Force Constant Calculations

a) Table 1 contains force constants calculated for several models. The "Rittner Potential" model includes interaction terms of charges and of induced dipoles. The equation used is a corrected form of Eq. (12) in Ref. [1], in which the expression for $k_b^{(I)}$ is given by:

$$k_b^{(I)} = -\frac{e^2 b^3}{l^3} \frac{\left\{1 + \frac{a^3}{l^3}\left[\frac{21}{4(1+a^3/(4l^3))} - \frac{2}{1+a^3/(8l^3)}\right]\right\}^2}{1 - \frac{2a^3 b^3}{l^6}\left(\frac{1}{1+a^3/(8l^3)}\right)}. \tag{1}$$

We take this opportunity to correct several other errors in Ref. [1].
The correct equations are (the numbers refer to [1]):

$$u_A = -\frac{ea}{l^2\cos\theta}\left(1 - \frac{a^2}{l^2} + \frac{a^4}{4l^4\cos^2\theta}\right)^{-\frac{1}{2}} - \frac{e}{2l\cos\theta} + \frac{ea}{l^2\cos\theta} - \frac{ea}{4l^2\cos^2\theta} + \frac{ea}{4l^2\cos^2\theta - a^2}, \tag{14}$$

$$V=\frac{e^2 a}{l^2\left[\left(1-\frac{a^2}{l^2}\right)\cos^2\theta+\frac{a^4}{4l^4}\right]^{\frac{1}{2}}}-\frac{e^2 a}{l^2\left(8\cos^2\theta-2\frac{a^2}{l^2}\right)}+\frac{e^2}{l\cos\theta}\left(\frac{1}{2}-\frac{a}{l}\right)+\frac{e^2 a}{8l^2\cos^2\theta}, \tag{17}$$

$$u_A=-\frac{e}{2l\cos\theta}+\frac{eb}{l^2[1+(2b^2/l^2)\cos 2\theta+b^4/l^4]^{\frac{1}{2}}}, \tag{20}$$

$$\frac{k_\delta}{l^2}=\frac{e^2}{8l^3}-\frac{e^2 b^3}{l^6(1+b^2/l^2)^3}. \tag{21}$$

The "Ion Multipole Potential" was calculated according to Eqs. (18) and (21) (as corrected). This model includes ion-induced multipole interaction terms.

The "Spherical Conductor Potential" is based on calculations according to Eq. (18) in Ref. [1] and the corrected form of Eqs. (12) and (21). From the sum of these three equations the first two terms of Eq. (22) (Ref. [1]) – i.e., overlapping terms which are of the charge-charge, and charge-induced dipole type – were omitted. This model includes all electrostatic interactions between polarisable ions.

The last column of Table 1 lists the experimental values of force constants available.

The polarizability values of the anion, α, and the cation, β, were taken from the polarizability value range, summarized by Eliezer [2]. The spread of experimental polarizability values is very large and none of the values is actually applicable to the group II halides. Thus the calculations can only show whether agreement with experiment can be obtained with polarizability values approximately within the experimental range.

In the calculations carried out in Ref. [1], it seems that all values are incorrectly multiplied by a factor of 2.3. This probably arises from the numerical factor of the electronic charge. In the course of the numerical calculations the equations are multiplied by a factor of $4.8^2/10$, to obtain proper dimensions. In the calculations in Ref. [1] this factor seems to have been unnecessarily squared.

b) From Table 1 it is seen that agreement between experiment and calculations exists for beryllium halides and magnesium chloride and the bromides and iodides of zinc and cadmium. We shall discuss this point in the conclusions.

The "Ion Multipole" model gives force constants closest to the experimental values (e.g. for BaF_2) in spite of the fact that the "Spherical Conductor Potential" model seems to be better, since it contains more interaction terms.

Another interesting point with reference to Table 1 is that the value of the cation polarizability, which gives the force constant closest to experiment, is usually the smallest one (higher cation polarizability values give smaller values of force constants). This fact would indicate that too high values of cation polarizability are being used. In this respect it is advisable to note that for the beryllium halides, where agreement is found between experiment and calculation, the cation polarizability is an order of magnitude smaller than the polarizabilities of the other cations.

Table 1. Bending force constant calculations

Molecule	l [Å]	α	β	Rittner potential	α	β	Ion multipole potential	α	β	Spherical conductor potential	$\frac{k}{l^2}$ exp
BeF_2	1.40	0.70	0.05	0.110	0.50	0.05	0.117	0.60	0.04	0.110	0.11[a]
$BeCl_2$	1.75	2.00	0.05	0.080	2.00	0.01	0.069	2.30	0.01	0.081	
$BeBr_2$	1.91	3.70	0.05	0.078	3.70	0.01	0.044	3.70	0.01	0.061	
BeI_2	2.18	5.70	0.05	0.057	5.70	0.01	0.029	5.70	0.01	0.041	
MgF_2	1.77	1.10	0.01	0.070	1.10	0.01	0.064	1.10	0.01	0.067	0.128[b]
$MgCl_2$	2.18	2.00	0.10	0.032	2.00	0.10	0.033	2.10	0.10	0.032	0.0317[a]
$MgBr_2$	2.34	3.70	0.10	0.031	4.20	0.01	0.029	5.00	0.01	0.034	
MgI_2	2.52	5.70	0.10	0.028	7.60	0.10	0.021	7.60	0.01	0.028	
CaF_2	2.10	0.50	0.30	0.023	1.10	0.30	0.030	0.50	0.30	0.025	0.0764[b]
$CaCl_2$	2.51	3.70	0.30	0.018	3.70	0.30	0.021	3.70	0.30	0.018	0.0306[a]
$CaBr_2$	2.67	5.00	0.30	0.017	5.00	0.30	0.018	5.00	0.30	0.016	
CaI_2	2.88	7.60	0.30	0.016	7.60	0.30	0.015	7.60	0.30	0.014	
SrF_2	2.20	0.50	0.70	0.010	1.10	0.70	0.022	0.50	0.70	0.015	0.0263[b]
$SrCl_2$	2.67	2.00	0.70	0.010	3.70	0.70	0.016	2.00	0.70	0.011	0.0208[a]
$SrBr_2$	2.82	3.70	0.70	0.009	5.00	0.70	0.014	3.70	0.70	0.010	
SrI_2	3.03	7.60	0.70	0.009	7.60	0.70	0.012	5.70	0.70	0.009	
BaF_2	2.32	0.50	1.50	−0.004	1.10	1.50	0.014	0.50	1.50	0.007	0.0148[b]
$BaCl_2$	2.82	2.00	1.50	0.003	3.70	1.50	0.011	2.00	1.50	0.006	
$BaBr_2$	2.99	3.70	1.50	0.003	5.00	1.50	0.010	3.70	1.50	0.005	
BaI_2	3.20	5.70	1.50	0.004	7.60	1.50	0.009	5.70	1.50	0.005	
ZnF_2	1.81	0.50	0.20	0.034	1.10	0.20	0.050	0.50	0.20	0.037	0.080[c]
$ZnCl_2$	2.05	3.70	0.20	0.034	2.90	0.20	0.039	2.00	0.20	0.029	0.052[c]
$ZnBr_2$	2.21	5.00	0.20	0.033	3.70	0.20	0.032	3.70	0.20	0.025	0.038[c]
ZnI_2	2.38	6.20	0.20	0.030	5.70	0.20	0.025	5.70	0.20	0.022	0.030[c]
CdF_2	1.97	1.10	0.10	0.039	1.10	0.10	0.042	1.10	0.10	0.039	0.063[c]
$CdCl_2$	2.21	3.70	0.10	0.038	3.70	0.10	0.033	3.70	0.10	0.033	0.050[c]
$CdBr_2$	2.37	5.00	0.10	0.034	5.00	0.10	0.027	5.00	0.10	0.028	0.037[c]
CdI_2	2.53	6.30	0.10	0.029	5.70	0.10	0.023	6.30	0.10	0.024	0.029[c]
HgF_2	2.08	0.50	0.30	0.023	1.10	0.30	0.031	0.50	0.30	0.025	0.139[c]
$HgCl_2$	2.29	3.70	0.30	0.022	3.70	0.30	0.028	2.00	0.30	0.021	0.089[c]
$HgBr_2$	2.41	5.00	0.30	0.021	5.00	0.30	0.024	3.70	0.30	0.019	0.070[c]
HgI_2	2.59	7.60	0.30	0.021	5.70	0.30	0.020	5.70	0.30	0.016	0.055[c]

l Bond length; α, β anion and cation polarizabilities.

[a] White, D.: Private communication. [b] Ref. [4]. [c] Ref. [3].

3. Convergence Tests

a) Table 2 examines the convergence of the models used to calculate force constants. The criterion for convergence chosen was expansion of the general expression in a multipole series and truncation of the expansion when agreement is reached between the general and expanded forms. To this end it was necessary to derive further terms to be added to Eq. (22) of Ref. [1], which are given by:

$$k_a^{(6)} + k_b^{(6)} = \frac{e^2}{l^{12}}\left(-\frac{697}{2048}a^9 - 2a^3b^6 - \frac{135}{16}a^6b^3 + 10b^9\right). \qquad (2)$$

The "Rittner Potential" is tested for convergence by expanding the abovementioned Eq. (12) into a multipole series up to l^{-9} and up to l^{-12}. The same is

Table 2. Convergence tests for multipole expansion

Molecule	Rittner up to l^{-9}	Rittner up to l^{-12}	Rittner potential	Ion multipole up to l^{-10}	Ion multipole up to l^{-12}	Ion multipole potential	Spherical conductor up to l^{-10}	Spherical conductor up to l^{-12}	Spherical conductor potential	Dipole quadrupole terms
BeF_2	0.120	0.109	0.110	0.118	0.117	0.117	0.118	0.110	0.110	−0.001
$BeCl_2$	0.087	0.078	0.080	0.075	0.072	0.069	0.097	0.084	0.081	−0.028
$BeBr_2$	0.090	0.075	0.078	0.061	0.053	0.044	0.085	0.067	0.061	−0.039
BeI_2	0.065	0.055	0.057	0.041	0.035	0.029	0.059	0.046	0.041	−0.029
MgF_2	0.070	0.069	0.070	0.065	0.064	0.064	0.068	0.067	0.067	−0.003
$MgCl_2$	0.033	0.032	0.032	0.033	0.033	0.033	0.033	0.032	0.032	−0.001
$MgBr_2$	0.032	0.031	0.031	0.031	0.030	0.029	0.039	0.035	0.035	−0.009
MgI_2	0.030	0.028	0.028	0.025	0.023	0.021	0.035	0.030	0.028	−0.013
CaF_2	0.023	0.023	0.023	0.030	0.030	0.030	0.025	0.025	0.025	0.000
$CaCl_2$	0.020	0.018	0.018	0.021	0.021	0.021	0.019	0.018	0.018	0.000
$CaBr_2$	0.018	0.017	0.017	0.019	0.018	0.018	0.018	0.016	0.016	0.000
CaI_2	0.017	0.015	0.016	0.016	0.015	0.015	0.016	0.014	0.014	−0.001
SrF_2	0.011	0.010	0.010	0.021	0.022	0.022	0.015	0.016	0.015	−0.002
$SrCl_2$	0.010	0.010	0.010	0.016	0.016	0.016	0.011	0.011	0.011	0.000
$SrBr_2$	0.010	0.009	0.009	0.014	0.014	0.014	0.011	0.010	0.010	0.000
SrI_2	0.011	0.009	0.009	0.012	0.012	0.012	0.010	0.009	0.009	0.000
BaF_2	−0.003	−0.004	−0.004	0.012	0.015	0.014	0.005	0.008	0.007	−0.004
$BaCl_2$	0.004	0.003	0.003	0.011	0.011	0.011	0.006	0.006	0.006	−0.001
$BaBr_2$	0.004	0.003	0.003	0.010	0.010	0.010	0.006	0.005	0.005	0.000
BaI_2	0.005	0.004	0.004	0.009	0.009	0.009	0.006	0.005	0.005	0.000
ZnF_2	0.035	0.034	0.034	0.051	0.050	0.050	0.038	0.037	0.037	0.000
$ZnCl_2$	0.045	0.032	0.034	0.042	0.040	0.039	0.033	0.029	0.029	0.001
$ZnBr_2$	0.042	0.031	0.033	0.034	0.033	0.032	0.032	0.025	0.025	−0.002
ZnI_2	0.036	0.028	0.030	0.029	0.027	0.025	0.030	0.022	0.022	−0.005
CdF_2	0.040	0.039	0.039	0.042	0.042	0.042	0.040	0.039	0.039	0.000
$CdCl_2$	0.041	0.037	0.038	0.036	0.034	0.033	0.038	0.033	0.033	−0.005
$CdBr_2$	0.036	0.033	0.034	0.030	0.028	0.027	0.033	0.029	0.028	−0.006
CdI_2	0.031	0.028	0.029	0.024	0.023	0.023	0.028	0.024	0.024	−0.006
HgF_2	0.023	0.023	0.023	0.031	0.031	0.031	0.025	0.025	0.025	0.000
$HgCl_2$	0.026	0.021	0.022	0.029	0.028	0.028	0.022	0.020	0.021	0.001
$HgBr_2$	0.026	0.021	0.021	0.026	0.025	0.024	0.022	0.019	0.019	0.000
HgI_2	0.026	0.020	0.021	0.021	0.020	0.020	0.020	0.016	0.016	−0.001

done for the "Ion Multipole Potential" by expanding the above-mentioned Eqs. (18), (21) into a multipole series up to l^{-10} and up to l^{-12}. Similar calculations are carried out using the "Spherical Conductor Potential". The expansion of the spherical conductor to l^{-10} is the above mentioned Eq. (22), and the expansion to l^{-12} includes in addition the term $k_a^{(6)} + k_b^{(6)}$ (Eq. (2)). The last column of Table 2 will be discussed in the next section.

b) The results in Table 2 show that in order to get force constants by a multipole expansion process, one has to carry out the expansion to terms in l^{-12} rather than to terms in l^{-10} (or l^{-9} in the case of the "Rittner Potential"). The l^{-12} interaction terms contribute a non-negligible contribution to the force constants. The contribution of these terms is always negative. The greatest relative contribution of these terms is found in the beryllium halides and in halides of zinc, cadmium and mercury.

The l^{-12} interaction terms, as calculated in Table 2, are important for the convergence of the multipole expansion. These terms bring the force constants, calculated by a multipole series, close to the force constants calculated by the general formula, for all molecules.

4. Dipole-Quadrupole Interaction Terms

a) As the convergence test necessitates a multipole expansion to terms in l^{-12}, it was decided to examine the contribution of l^{-11} terms, which describe an induced dipole-induced quadrupole interaction. In order to derive the relevant term the following procedure was used: First, the tensor components of the dipole-induced quadrupoles in the anion and cation points were evaluated. Then the potentials arising from the induced quadrupole components were evaluated. The potentials were substituted in the general potential equation (Eq. (9) of Ref. [1]). The resulting equation was differentiated twice and θ was set at zero. Division by $4l^2$ and expansion in series, retaining only l^{-11} terms, finally gives the expression:

$$k_a^{(5)} + k_b^{(5)} = \frac{e^2}{l^{11}}\left(-\frac{85}{128}a^8 + \frac{207}{16}a^5 b^3 - \frac{735}{32}a^3 b^5\right). \tag{3}$$

b) The results of Eq. (3) are given in the last column of Table 2. For most molecules this term contributes a small but finite contribution. Note that the main contributions of this term to the force constants are negative. The most pronounced effect is observed in the beryllium halides. This term contributes less to the force constants of the calcium and strontium halides. It may be concluded that when carrying out a multipole expansion for force constant calculation, it is desirable to include the induced dipole-induced quadrupole term.

5. Summary and Conclusion

Calculations with the so-called polarized-ion model were carried out for linear triatomic molecules in the gas phase. When calculating force constants by carrying out a multipole expansion it is necessary to include terms up to l^{-12}.

The validity of such a model is tested by comparison of the calculational results with experiment. As was mentioned above agreement is obtained for only part of the group II metal halides. One reason is that the theoretical treatment developed above is applicable only to linear molecules and serious difficulties arise when attempts to extend it to bent molecules are made. It was suggested recently (see Discussion in Ref. [2]) that the magnesium, calcium and strontium fluorides, strontium cloride and all the barium halides are bent. And, indeed, the experimental values for these do not agree with our calculations. However, calcium chloride is apparently linear but still no agreement is found. Nor is there any agreement in the case of the mercuric halides. In the case of the mercuric halides there are probably special factors at work, as discussed in Ref. [2]. However, a general reason for lack of agreement may be that the experimental values of the force constants were determined from vibrational frequencies measured in inert gas matrices [3, 4] and not in the gas phase. Similarly, the polarizability values taken for the force constant calculations were determined from values measured in crystals [5, 6], or in water solutions [7]. These values are not necessarily the correct ones for determining bending force constants. This point is reinforced by the wide spread of the polarizability values, as measured by different investigators (see table in Ref. [2]).

Although the agreement between theory and experiment is not too good at present, we believe the present method leads to a useful comparison of theoretical and experimental force constants, should reliable experimental measurements (see above) become available.

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