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Commentationes

The Polarized Ion Model and the Bending Force Constants of the Group IIB Halides

I. ELIEZER

Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel

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The applicability of the polarized ion model to the bending force constants of the group II metal dihalides is examined. Calculations are carried out for zinc, cadmium and mercury halides and show that the force constant values obtained are insensitive to the anion polarizability values used, but are quite sensitive to the metal ion polarizability values. It is shown that available polarizability values are not applicable to the group II dihalides. Therefore, force constant calculations with the metal ion polarizability as a variable parameter are carried out. Results agreeing with experimental values of the bending force constants are obtained for reasonable polarizability values, except for the case of the mercury halides. This discrepancy is discussed.

Die Anwendbarkeit des polarisierten Ionenmodels zur Berechnung der Kraftkonstanten der Beugungsschwingung bei Metalldihalogeniden der Gruppe II wird untersucht. Berechnungen für Zink-, Cadmium- und Quecksilberhalogeniden werden durchgeführt und zeigen, daß die Werte für die Kraftkonstanten nur schwach von der Polarisierbarkeit der Anionen, dagegen ziemlich stark von der Polarisierbarkeit der Metallionen abhängen. Weiter wird gezeigt, daß die in Betracht kommenden Polarisierbarkeiten für die Dihalogenide der Gruppe II zu keinen sinnvollen Ergebnissen führen. Deshalb wurden die Berechnungen mit der Metallionen-Polarisierbarkeit als variablem Parameter ausgeführt. Resultate, die mit den experimentellen Werten übereinstimmen, wurden für vernünftige Polarisierbarkeiten erhalten. Die Quecksilberhalogenide bilden eine Ausnahme, die diskutiert wird.

Examen de l'applicabilité du modèle de l'ion polarisé pour le calcul des constantes de force de déformation des dihalogénures des métaux du groupe II. Des calculs sont effectués pour les halogènures de zinc, cadmium et mercure, montrant que les valeurs obtenues pour les constantes de force sont insensibles aux valeurs des polarisabilités de l'anion, mais sont assez sensibles à celles de l'ion métallique. On montre que les polarisabilités disponibles ne sont pas applicables aux dihalogènures du groupe II. De ce fait les calculs de constante de force sont menés avec la polarisabilité variable pour l'ion métallique. Des résultats en accord avec les valeurs expérimentales des constantes de force de déformation sont obtenues pour des valeurs raisonnables de la polarisabilité, sauf dans le cas des halogènures de mercure. Cette discordance est discutée.

Introduction

The polarized ion model, or ionic model, was introduced two decades ago [1] and has since then been applied to many systems [2–14]. Its advantages are simplicity, tractability and ease of picturization. Its disadvantages are claimed to be oversimplification and inability to describe systems which include factors other than electrostatic and polarization interactions. Despite these apparent drawbacks, it has proved surprisingly successful in treating the varied problems mentioned above. One of the subjects to which it has been applied is the structure of the group II metal dihalides and the conclusion has been put forward that it is unsuitable for dealing with this problem. Recently some new data have become available on the structure of these halides and these prompted a re-examination of the applicability of the polarized-ion model to the group II halides which is the subject of this study.

The group II halides of both A and B subgroups (except perhaps for the Be halides) are often used as textbook examples of linear molecules. An examination of the experimental data on which these conclusions are based shows that these data do not exclude the possibility of bent structures in some cases. Thus, for example, electron diffraction experiments [15–17] are often quoted as proof of linearity. However, although the angles in these studies are given as 180° their uncertainty is in some cases as large as ±40° so that these results do not preclude an angle of up to 140° at the central atom, i.e., a bent molecule.

One quantitative application of the polarized ion model to the structure of these compounds has been in the calculations of the bending force constants of these molecules from electrostatic energy considerations derived on the basis of the model.

Initially [18] the applicability of the ionic model to the group II halides was discounted because it was assumed that such a model leads to zero bending mode frequencies. Although this assumption was later disproved [19], only order of magnitude values for the vibrational frequencies of the group II halides were obtained. However, these calculations overlooked the vector character of the induced dipoles in the molecules treated. Nevertheless, the conclusion of more sophisticated of calculation [20, 21] was again, that the polarized ion model cannot account for the observed bending frequencies of the group II dihalides.

Theoretical

The original presentation of the ionic model [1] considered its application to the NaCl molecule and consisted of the representation of Na^+ and Cl^- ions as tangentially touching charged spheres. It can be shown that such charged spheres are equivalent to point charges insofar as the electrostatic fields generated are concerned. The polarization of each ion in the field of the other is represented by a point dipole at the centre of the sphere and the resultant final fields can then be calculated. The repulsion forces are represented by exponential terms. The model was used initially to calculate the dipole moments, ionicity and binding energy of the alkali halides. It was later used [6, 11, 12] to obtain the electrostatic energies and stabilization constants of the group IIB dihalides. Known as the Rittner model, it expresses the electrical deformation of the ions by including only the dipole polarizabilities. This is of course an incomplete description. To describe the system more fully we should include all higher multipoles and the interaction they give rise to. Obviously, however, at some point, the inclusion of higher terms will lead to insignificant changes in the results and the problem is to decide where this cutoff point is. By significant we can mean either the number of figures necessary for other calculations or the number of figures which is meaningful for comparison with experimental results. Of course, proper convergence should be demonstrated.

The early calculations of force constants of the group II halides [19] included only the anion dipole polarizabilities. Poor agreement with the experimental values was obtained, but it could be attributed to the incorrect treatment of the dipole forces mentioned above. Nevertheless it is clear that the cation polarizability should be taken into account, because the polarization effects may produce directional bond properties, i.e. the position of minimum energy for the system can be nonlinear with an angle determined by a balance between repulsion of the anions, driving them apart, and a tendency for the anions to be close together so that their electric fields add vectorially. Such polarization lowers the energy and corresponds to a negative contribution to the force constant. Obviously this effect will be of greater importance the larger and more polarizable the central ion is.

In later calculations [20] a proper vectorial treatment was given and cation polarizabilities were included. Also, considerably more polarization terms were included in addition to the charge-charge term, i.e. charge-dipole, charge-quadrupole and dipole-dipole. The dipole-quadrupole and quadrupole-quadrupole terms were also calculated but other terms of comparable order such as the charge-octopole and dipole-octopole terms were omitted because of lack of data on octopole polarizabilities. The terms included also omit considerations such as the fact that the fields determining the dipole-dipole terms are due to ions with induced dipoles and similarly for the charge-quadrupole terms. It was brought out at this stage that allowance should be made for saturation of metal ion polarizabilities. The importance of this will become clear in the next section.

It is usually thought (and this is the reason for the name "ionic" model) that the higher terms beyond charge-charge and charge-dipole interaction decrease rapidly and are of little importance. That this is not true and that higher terms are much more important than generally supposed can be seen from looking at results in Ref. [20]. It then becomes clear that not only are dipole-dipole interactions important but that the quadrupole terms: "charge-quadrupole" and even "dipole-quadrupole" are quite large. In fact, they can be larger than dipole-dipole terms and even charge-dipole terms.

A perennial objection to the polarized ion model is that it is unable to take account of the covalency of the molecule. It is true that "polarized ion" functions are quite different than "ionic + covalent" functions, but, as has been pointed out, either set being complete must ultimately provide a correct molecular wave function so that in any given problem the choice between the two is one of convenience and of rapidity of convergence. In other words the "polarized-ion" model is in the limit identical to the "ionic + covalent" model.

Another claim that has been made is that the repulsion between the anions due to distortion effects is greater than a polarized ion would predict. There is no proof, as yet, that this is a valid argument.

However, there are still several deficiencies in the model. One is the treatment of multipole interactions as though charge distributions do not overlap. Obviously, interionic penetration can be appreciable, the more so the larger the ions. To some extent such interpenetration is implicitly taken into account in the polarizability values used, but the meaning of polarization of overlapping charge distributions is far from clear. Further weaknesses are incomplete treatment of multipole terms, the saturation effects problem and the arbitrary assumption of the applicability of polarizability values such as Sternheimer's quadrupole polarizability results [22–23] (although it is known that Sternheimer's calculations for dipole polarizabilities with the same methods give results far from the experimental values).

A further treatment [21] was occasioned not by the above defects but rather because the method in Ref. [20] was thought to lead almost inevitably to algebraic errors. Nevertheless, the expressions obtained resemble those in Ref. [20] rather closely. This treatment was really justified by the fact that more data had become available. In it charge-octopole effects were calculated, but it omitted the dipole-quadrupole and quadrupole-quadrupole terms included previously. A comparison of calculations based on the "point charge" model, the "Rittner" model, and the "spherical potential" model (which includes the higher polarization terms mentioned above), with experimental results (available at the time) showed poor agreement, which would indicate that the model is not a good representation of the molecule and so the bonding in the molecules must be largely covalent. However the covalent models available also provided a poor description and it was finally concluded that no satisfactory description of group II halides is available.

The conclusion on the nonvalidity of the polarized ion model is immediately challenged, however, when the following points are noted: To test convergence, an estimate was made of the terms not included in the expression for the force constants (truncated multipole expansion). These "remainder terms" make the results for molecules with small bond lengths and large polarizabilities meaningless, e.g. for $\mathrm{Be\,I_2}$ while the calculation gives $K_\delta/l^2 = 0.146\,md/\text{Å}$ the remainder terms are estimated to be -0.162, i.e. their inclusion would lead not just to a change in value but to a change in sign, i.e. to a negative force constant. Also, as a result of the high polarizabilities of the metal ions, the remainder terms for $\mathrm{CdF_2}$, $\mathrm{CdBr_2}$, $\mathrm{HgBr_2}$ and $\mathrm{HgJ_2}$ are larger than the calculated values thus rendering these too meaningless, while for $\mathrm{ZnBr_2}$, $\mathrm{ZnI_2}$, and $\mathrm{CdCl_2}$ the results are also doubtful due to large remainder terms. Nevertheless, it is true that the quantities involved for the IIB group are small and the neglected terms should not affect a discussion of the results in terms of order of magnitude.

The most important point concerns the parameters used. For the dipole polarizabilities of the halide ions, the values derived from the observed dipole moments of the lithium halides were used. However, these values were specifically obtained to fit the lithium halide case [24, 25] and differ from experimental values obtained from e.g. refractivities. This was due to the recognition of the dependence of polarizability on field strength. But for this very reason the halide polarizability values for lithium halides are not applicable to the group II halides. The same applies to the metal ion polarizabilities which usually are refractivity values. These were reduced for some metals to account for saturation effects, but in an entirely arbitrary fashion. Furthermore, in order to obtain quadrupole and octopole polarizabilities, the relations $\alpha_d = r^3$, $\alpha_q = r^5$ and $\alpha_o = 2r^7$ were used (α = polarizability, d = dipole, q = quadrupole, o = octopole) – again a somewhat arbitrary assumption.

The last remark concerns the statement [21] that the mercuric halides show that covalent bonding is not necessarily associated with high bending force constants. It has been shown very recently [26] that indeed it is.

Results and Discussion

Despite all the above weaknesses, the discrepancy between experiment and theory for the zinc halides was so serious – a whole order of magnitude (while the convergence of the expansion for zinc chloride at least was good) that this did seem to pose a serious objection to the model and/or the calculational approach. Very recently, however, some new results for the group IIB halides became available [26, 27, 35], prompting a re-examination of the calculations, and of the applicability of the polarized-ion model. The important fact brought out in the new results is that the experimental zinc halide values, on which previous comparisons were based, were quite incorrect. As this was the main reason for the conclusion of the inapplicability of the polarized ion treatment to group IIB halides, this conclusion obviously did not hold any more.

However, this was also an opportunity to introduce a different approach to the use of the polarized model. It should be clear from the previous section that terms including multipoles (higher than dipoles) which give a sizeable contribution to the calculations of the force constants have been neglected. Therefore, it seemed worthwhile to carry out a multipole expansion recalculation based on a reasoned inclusion of all terms of detectable influence. This would mean, according to the previous section, all terms to which multipoles up to and including octopoles contribute. Although seemingly the correct thing to do, it turned out that this is not the case. The reason for this is the parameters used and in particular the polarizability values. The approach to the selection of these values has been incorrect so far, and its influence on the results of the calculations is important. As mentioned in the previous section, the values used for cation and anion polarizabilities in the group II halides are at best approximations, and one could almost say estimates. This is due to the fact that the polarizability is a quantity which is very sensitive to environment and therefore values obtained for the polarizability apply only to the case for which they were obtained and cannot be used in other cases. In some cases where the polarized ion model has been used, such as calculations of equilibrium constants of reactions, it turned out that the value of the quantity calculated was not sensitive to changes in the polarizabilities of the various particles of the system [11, 12], so that in such cases an approximation or estimate is acceptable and gives reasonably accurate results. However, the above argument does not apply to force constant calculations. When the author tried the calculations with different polarizability values, it was found that the sensitivity to anion polarizability was small but changes in the metal ion polarizability changed the values calculated for the force constants considerably. Therefore, efforts were made to obtain reliable polarizability values applicable to the group II halide systems. It was found that at the present, no such values are available. Table 1 shows the large spread of polarizability values given in the literature but even so *none of these values in Table 1 is actually applicable to the*

Table 1. *Spread of experimental polarizability values*

Ion	α_d, Å^3
F^-	0.76 –1.04[a]
Cl^-	2.17 –3.66[a, b]
Br^-	3.7 –4.97[b, c, d, e, f, g]
I^-	5.7 –7.55[b, c, d, e, f, g]
Be^{+2}	0.007–0.04[a]
Mg^{+2}	0.0943[h]
Ca^{+2}	0.44 –1.1[a, f]
Sr^{+2}	0.84 –1.6[d, e, f, h]
Ba^{+2}	1.56 –2.5[d, e, f, h]
Zn^{+2}	0.28 –0.8[d, e, h]
Cd^{+2}	1.09 –1.8[d, e, h]
Hg^{2+}	0.5 –3.18[e, i, j]

[a] Ref. [22]. — [b] Ref. [25]. — [c] Ref. [24].

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group II halides. This led to the inevitable conclusion that the polarized ion model can be tested in cases sensitive to polarizability values only when the polarizability is taken as a variable parameter. Therefore, calculations were undertaken with α as a variable parameter to see whether on variation within reasonable limits, a value of α can be obtained for which agreement with experiment can be found. It should be stressed again that the value of α *should not* necessarily be in the range given in Table 1.

As the equilibrium configuration of the group II A dihalides is rather controversial at present [28–33], and, in addition, experimental results on these are very scanty, they are not treated in the present paper. Thus the calculations assume a linear equilibrium configuration and apply to group II B halides only. The relevant results are presented in Table 2 which compares these calculations with the experimental results available. Two calculated values are included for zinc chloride to exemplify the sensitivity of the results to changes in metal ion polarizability values. Twin sets of values are given for cadmium and mercury halides to show the insensitivity to anion polarizabilities. It is clear from Table 2 that agreement is obtained for all zinc and cadmium halides with values which are no less applicable than those in Ref. [20] or [21] *for use in the group II B halides.* On the other hand, no such agreement could be obtained for the mercury halides.

As an interesting aside, Table 2 also includes recent experimental estimates of the force constants for beryllium [34] and magnesium [32] fluorides. When compared with the theoretical results (Table 2), it is seen that the agreement for

Table 2. *Comparison of calculated and experimental bending force constants*

	α_M	α_A	k_δ/l^2 (calculated)	k_δ/l^2 (experimental[a])
ZnF_2	0.25	0.497	0.079	0.080
$ZnCl_2$	0.3	2.17	0.061	0.051
	0.4	2.17	0.045	
$ZnBr_2$	0.5	4.15	0.035	0.036
ZnI_2	0.6	6.24	0.030	0.029
CdF_2	0.3	0.497	0.064	0.063
	0.3	1.0	0.063	
$CdCl_2$	0.4	2.17	0.046	0.049
	0.4	2.8	0.046	
$CdBr_2$	0.5	4.15	0.038	0.039
	0.5	3.7	0.037	
CdI_2	0.6	6.24	0.033	0.029
	0.6	5.7	0.032	
HgF_2	0.25	0.497	0.062	0.139
	0.25	1.0	0.063	
$HgCl_2$	0.25	2.17	0.055	0.088
	0.25	2.8	0.057	
$HgBr_2$	0.25	4.15	0.055	0.070
	0.25	3.7	0.053	
HgI_2	0.25	6.24	0.050	0.055
	0.25	5.7	0.049	
BeF_2	0.0079	0.497	0.307[b]	0.11[c]
MgF_2	0.943	0.497	0.114[b]	0.14[d]

[a] Refs. [26, 27]. — [b] Ref. [21] Corrected. — [c] Ref. [34]. — [d] Ref. [32].
M = Metal ion, A = anion.

beryllium fluoride is much better than in Ref. [21], while the disagreement between theory and experiment for the magnesium halides, thought to exist in Ref. [21], is not really there, at least for magnesium fluoride. However, it must be mentioned that although MgF_2 was found to be linear in Ref. [29], this was disputed in Ref. [32] but reconfirmed in Ref. [33]. Should Ref. [32] prove to be correct, the present calculation is, of course, inapplicable, but the conclusion [21] that there is disagreement between theory and experiment for the magnesium halides is still groundless, because then it is based on the assumption of an incorrect equilibrium configuration.

To come back to the group IIB halides, we see that within present day knowledge and capabilities the polarized ion model can account for most of the available experimental results on the bending force constants, or at the very least, cannot be dismissed as unable to account for them until really reliable polarizability values become available. Then, fuller multipole expansion calculations should be made. Obviously, without such polarizability values, no such extensions are worthwhile. However, the present results do indicate, contrary to previous conclusions, that when carefully applied, the polarized ion model is still a useful tool even in its present state, and it is the author's opinion that its extended use should prove rewarding.

There still remains the question of the mercury halides. There are two possibilities. Either the polarized ion approach is inapplicable (here again this might be due to inaccuracy of the model or of the calculations), or the experimental results are deficient. The argument for the first case is the often given one of the considerable covalency of the HgX_2 compounds. As discussed in the previous section, calculations using a complete set of polarized ion functions should be applicable to HgX_2 even if largely covalent, but such a set has certainly not been used in the present, or any previous, calculations. The arguments for the second case are a) that calculations of stability constants of HgX_2, using the same model give good agreement with experiment [11, 12], b) that experimental results on HgX_2 do not agree among themselves and are in a region difficult to measure which has only recently become accessible. Even the latest results which occasioned our resumption of interest in the problem were done in matrices in which the ν_2 value obtained depends on the environment to some extent.

The question of HgX_2 must therefore remain open until reliable gas phase values become available and, of course, until a more reliable (parameterwise) and complete calculation can be made.

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Professor I. Eliezer
Department of Chemistry
Tel-Aviv University
Ramat-Aviv
Tel-Aviv, Israel