

Dipole moment and molecular constants for copper and silver monohalides

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Abstract : The dipole moment and the spectroscopic constants for the copper and silver monohalides have been calculated using Rittner, Truncated Rittner (TR) and Ionic models. A comparison of these calculated parameters with the experimentally measured values indicates that though the molecular constants predicted by the three models are nearly identical, TR model predict a more realistic value of dipole moment for these monohalides.

Keywords : Dipole moment, copper and silver monohalides, model potential, spectroscopic constants.

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1. Introduction

There are several model potentials known to describe the structure and properties of ionic molecules (see Varshni and Shukla 1961). The suitability of these models in general have been tested by calculating the molecular parameters in the case of alkali monohalides. Out of these several models the model proposed by Rittner (1951) is supposed to be most suitable one. In this potential the ions are assumed to be polarizable spherical charge distribution. The Rittner potential is given as

$$U_{Ritt}(r) = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} - \frac{c}{r^6} + A \exp\left(-\frac{r}{\rho}\right) \quad (1)$$

where, r is the internuclear distance and α_1, α_2 are the polarizabilities of the metal and halogen ions respectively. The parameter A in the repulsive term can be approximated simply as a constant. The constant c in the Van der Waals term have been evaluated by using the London approximation

$$c = \frac{5}{2} \alpha_1 \alpha_2 (I_1 I_2) / (I_1 + I_2) \quad (2)$$

where I_1 and I_2 are the ionization potentials of the two free ions. The values of A , and c can be evaluated by applying the boundary conditions and using the known molecular constants. According to Rittner (1951) this model should give an

accurate value of the dipole moment and spectroscopic constants for the molecule which satisfies the condition

$$r^6 \gg 4\alpha_1\alpha_2. \quad (3)$$

It is found that in the case of alkali halides, this condition is fully satisfied. However, there are many more ionic molecules in which this condition is not fulfilled. For example in the case of alkaline earth monohalides, the polarizability of alkaline earth ions are so large compared to alkali ions, that the condition for the applicability of Rittner model to this group of molecules seems not justified.

The dipole moment calculated using this model in most of the molecules, comes out either very small or negative. It has been pointed out that this is due to over-estimation of the polarization effect in Rittner model (1951). Brumer and Karplus (1973) proposed another model in which contribution of induced moment due to the polarizing field has been neglected. This so called 'Truncated Rittner Model' potential can be expressed as

$$U_{\text{TRitt}}(r) = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{c}{r^6} + A \exp\left(-\frac{r}{\rho}\right) \quad (4)$$

and the net dipole moment as

$$\mu_{\text{TRitt}} = e \cdot r - \frac{e(\alpha_1 + \alpha_2)}{r^2}.$$

Torring et al (1984) calculated the dipole moment for the alkaline earth monohalides using this model. They found that the Truncated Rittner model gives reasonably better value of dipole moment but only for a few alkaline earth monohalides. Therefore, they developed a new model potential which takes into account the large charge-shift in the metal ion arising from the polarization and named it as 'Ionic model'. In alkaline earth monohalides, the metal ion consists of a closed shell Me^{++} nuclei with a single s electron in the valence shell. The polarizability of the doubly charged nucleus may be neglected. So the polarization of ion is entirely due to s-p-d hybridization of the single valence electron. This means electron centre of charge must be shifted by Δr to give the induced dipole moment

$$\mu^+ = e \cdot \Delta r.$$

Therefore in the new model, Torring et al (1984) used Rittner's treatment for the polarization of halogen ion. The complete polarizing field arises due to superposition of the field from Me^{++} nucleus, at distance r and valence electron at distance $(r + \Delta r)$ respectively. As a result of this, the induced moment due to halogen ion comes out in the form of

$$\mu^- = \alpha_2 \left(\frac{2e}{r^3} - \frac{e}{(r + \Delta r)^3} \right). \quad (5)$$

Here Me^{++} nucleus is treated as spherical charge distribution since its polarizability have been neglected. It means some higher order term have been neglected even in this model but larger contribution due to charge-shift Δr is taken into account. So the induced moment μ^+ is given as

$$\mu^+ = e \cdot \Delta r = \alpha_1 \left(\frac{e}{(r + \Delta r)^2} + \frac{2\mu^-}{(r + \Delta r)^3} \right). \quad (6)$$

Inserting eq. (5) into eq. (6) we get

$$\Delta r = \frac{\alpha_1}{(r + \Delta r)^3} + \frac{4\alpha_1\alpha_2}{r^2(r + \Delta r)^3} - \frac{2\alpha_1\alpha_2}{(r + \Delta r)^5}. \quad (7)$$

From these, the ionic model is given as

$$U_{\text{ionic}}(r) = -\frac{2e^2}{r} + \frac{e^2}{(r + \Delta r)} + \left(\frac{\mu^+}{2\alpha_1} \right)^2 - \left(\frac{\mu^-}{2\alpha_2} \right)^2 - \frac{c}{r^6} + A \exp\left(-\frac{r}{\rho}\right) \quad (8)$$

where Δr is the charge shift. For alkaline earth monohalides, Torring *et al* (1984) found the value of Δr of the order of 1 Å which is not very small compared to r and therefore it can not be neglected. They calculated the ground state dipole moment and spectroscopic constants for alkaline earth monohalides using this model as well as Rittner and Truncated Rittner models and compared the results with available experimental data. It was found that ionic model represents the dipole moment in a better way for these molecules compared to the other two models.

This encouraged us to use all the three models described above for the calculation of the ground state dipole moment and spectroscopic constants i.e. α_e , and $\omega_e x_e$ in the case of IB group monohalides (copper and silver monohalides), to see their suitability for these molecules. Results obtained are compared with available experimental data in different tables.

2. IB group monohalides

The copper and silver monohalides are very similar to alkali monohalides and therefore Rittner potential (1951) should reproduce the experimental values for these molecules. However, the basic condition for Rittner potential i.e. $r^6 \gg 4\alpha_1\alpha_2$ does not hold good for these molecules. For copper and silver halides this value is nearly one fourth of the alkali halides. Of course, in copper and silver halides the metal ion M^+ and halogen X^- ion form close-cell systems and apparently there does not appear any charge-shift. However, in the metal ion the electrons in d orbital particularly in the $nd\sigma$ orbital whose energy is nearly equivalent to $(n+1)s$ are very loosely bound compared to those in np orbital in halogen ions. Therefore, a small charge-shift in these cases are also expected. We calculated the charge-

shift for these molecules and found that Δr for them to have appreciable magnitude (see Table 2). Therefore, it was thought worthwhile to evaluate the molecular parameters for these molecules using ionic as well as Rittner and Truncated Rittner models and check the suitability of the three.

One important parameter used in these calculations which is also a source of major error, is the polarizability of ions. The polarizability value for different ions have been given by Pauling (1927) and more recently by Coker (1976) and Sangachin and Shanker (1989). Most of earlier calculations have been made using the values given by Pauling (1927). Pauling's value refer either the crystalline state polarizability or free ion polarizability. Therefore, the values calculated using these values either underestimate the dipole moment or sometimes give negative value. Fajon and Joos (1924) have shown that the electronic polarizability of cation is slightly increased and of anion is decreased during molecule formation. A more recent view about this is that in the bonded system the polarizability of cation remains unchanged whereas of anion is reduced significantly (Wilson and Curtis 1970, Coker 1979). Nevertheless, the polarizability of anion will also depend on environment (Kumar *et al* 1986, Sangachin and Shanker 1989). The polarizability data used in the present calculation are given in Table 1. In

Table 1. Values of free and molecular state polarizability for metal and halogen ions.

Molecules	Polarizability $\times 10^{-24} \text{ cm}^3$	
	Metal	Halogen
CuF	0.43	1.01 ^a , 1.05 ^b , 1.38 ^c
CuCl	0.43	3.30 ^a , 3.69 ^b , 3.94 ^c
CuBr	0.43	4.51 ^a , 4.81 ^b , 5.22 ^c
CuI	0.43	6.68 ^a , 7.16 ^b , 7.81 ^c
AgF	1.72	1.01 ^a , 1.05 ^b , 1.38 ^c
AgCl	1.72	3.32 ^a , 3.69 ^b , 3.94 ^c
AgBr	1.72	4.55 ^a , 4.81 ^b , 5.22 ^c
AgI	1.72	6.73 ^a , 7.16 ^b , 7.81 ^c

^aMolecular state polarizability

^bPauling's value of polarizability

^cCoker's value of polarizability

the present paper we have used three sets of polarizabilities suggested by Pauling (1927), Coker (1979) and Sangachin and Shanker (1989) and calculated the dipole moment and molecular parameters using the three models.

3. Molecular constants

For calculation of spectroscopic constants, i.e. α_e and $\omega_e x_e$, one needs to evaluate

the value of repulsive parameter ρ and the Van der Waals constant C . Varshni and Shukla (1963) have given following conditions to hold good for any potential $U(r)$

$$\left(\frac{dU(r)}{dr}\right)_{r_e} = 0 \quad (9)$$

and

$$\left(\frac{d^2U(r)}{dr^2}\right)_{r_e} = K_e \quad (10)$$

Solving these two equations we get the expression for ρ in terms of known parameter, from which ρ could be evaluated. The force constant K_e have been

Table 2. Calculated values of charge-shift Δr and force constant K_e .

Molecules	Charge shift $\Delta r \times 10^{-10}$ cm	Force constant $K_e \times 10^3$ dyne/cm	$r^0/4 \epsilon_1 \epsilon_2$
CuF	0.1671 ^a	3.331	15.633 ^a
	0.1654 ^b		16.253 ^b
	0.1804 ^c		11.895 ^c
CuCl	0.1666 ^a	2.308	11.728 ^a
	0.1592 ^b		13.114 ^b
	0.1713 ^c		10.984 ^c
CuBr	0.1574 ^a	2.043	12.725 ^a
	0.1535 ^b		13.572 ^b
	0.1634 ^c		11.726 ^c
CuI	0.1511 ^a	1.733	13.263 ^a
	0.1461 ^b		14.215 ^b
	0.1578 ^c		12.158 ^c
AgF	0.3937 ^a	2.504	8.417 ^a
	0.3911 ^b		8.750 ^b
	0.4145 ^c		6.404 ^c
AgCl	0.4010 ^a	1.830	5.533 ^a
	0.3840 ^b		6.150 ^b
	0.4095 ^c		5.182 ^c
AgBr	0.3908 ^a	1.677	5.674 ^a
	0.3836 ^b		5.998 ^b
	0.4021 ^c		5.228 ^c
AgI	0.3883 ^a	1.457	5.503 ^a
	0.3792 ^b		5.855 ^b
	0.4019 ^c		5.045 ^c

^aCalculated with Pauling's value of polarizability for halogen

^bCalculated with molecular state value of polarizability for halogen

^cCalculated with Coker's value of polarizability for halogen

evaluated using expression $4\pi^2\mu\omega_e^2c'$ where ω_e is the vibrational frequency and μ is the reduced mass and c' is the velocity of light. The values of ρ , K_e and c thus obtained using three models for the three polarizability values are given in the Table 3. The molecular constants α_e and $\omega_e x_e$ are given as

Table 3. Calculated values of repulsive parameter ρ , and Van der Waals constant C.

Molecules	$\rho \times 10^{-8}$ from Rittner	$\rho \times 10^{-8}$ from T-Rittner	$\rho \times 10^{-8}$ from Ionic	Van der Waals constant $C \times 10^{-60}$ erg/mol
CuF	0.2058 ^a	0.2196 ^a	0.2031 ^a	6.72 ^a
	0.2126 ^b	0.2119 ^b	0.2030 ^b	5.51 ^b
	0.2126 ^c	0.2261 ^c	0.2054 ^c	7.53 ^c
CuCl	0.2525 ^a	0.2621 ^a	0.2184 ^a	18.26 ^a
	0.2575 ^b	0.2575 ^b	0.2171 ^b	16.33 ^b
	0.2637 ^c	0.2648 ^c	0.2139 ^c	19.50 ^c
CuBr	0.2797 ^a	0.2735 ^a	0.2212 ^a	22.95 ^a
	0.2705 ^b	0.2703 ^b	0.2200 ^b	21.515 ^b
	0.2764 ^c	0.2796 ^c	0.2220 ^c	24.90 ^c
CuI	0.2935 ^a	0.2937 ^a	0.2262 ^a	32.58 ^a
	0.2900 ^b	0.2898 ^b	0.2252 ^b	30.393 ^b
	0.2977 ^c	0.2984 ^c	0.2275 ^c	35.534 ^c
AgF	0.2462 ^a	0.2457 ^a	0.2349 ^a	22.930 ^a
	0.2455 ^b	0.2501 ^b	0.2320 ^b	22.053 ^b
	0.2500 ^c	0.2506 ^c	0.2377 ^c	30.133 ^c
AgCl	0.2875 ^a	0.2883 ^a	0.2651 ^a	73.06 ^a
	0.2777 ^b	0.2849 ^b	0.2632 ^b	65.730 ^b
	0.2892 ^c	0.2904 ^c	0.2661 ^c	78.000 ^c
AgBr	0.2891 ^a	0.2866 ^a	0.2529 ^a	91.79 ^a
	0.2870 ^b	0.2890 ^b	0.2517 ^b	86.825 ^b
	0.2920 ^c	0.2900 ^c	0.2547 ^c	99.61 ^c
AgI	0.3073 ^a	0.3047 ^a	0.2598 ^a	130.310 ^a
	0.3015 ^b	0.3014 ^b	0.2584 ^b	122.484 ^b
	0.3109 ^c	0.3090 ^c	0.2623 ^c	142.139 ^c

^aCalculated from Pauling's value of polarizability for halogen

^bCalculated from molecular state polarizability for halogen

^cCalculated from Coker's value of polarizability for halogen

$$\alpha_e = - \left[\frac{Xr_e}{3} + 1 \right] \frac{6B_e^2}{\omega_e^2}$$

$$\omega_e x_e = \left[\frac{5X_e}{3} - \gamma \right] r_e^2 \cdot \frac{W}{r_e^2 \mu_d}$$

where

$$X = \frac{d^3U(r)}{dr^3} / \frac{d^2U(r)}{dr^2},$$

$$Y = \frac{d^4U(r)}{dr^4} / \frac{d^3U(r)}{dr^3}$$

and

$$W = 2.1078 \times 10^{-16}.$$

Using these expressions for the three potentials, the α_0 and $\omega_0 x_0$ have been

Table 4. Calculated values of dipole moment for Cu and Ag monohalides.

Molecules	μ in Debye from littner	μ in Debye from T-Rittner	μ in Debye from Ionic model	Expt. value of μ in Debye
CuF	5.31 ^a	6.05 ^a	5.648 ^a	5.7
	5.41 ^b	6.11 ^b	5.72 ^b	
	4.49 ^c	5.53 ^c	4.95 ^c	
CuCl	3.84 ^a	5.18 ^a	4.238 ^a	
	4.43 ^b	5.59 ^b	4.81 ^b	
	3.38 ^c	4.86 ^c	3.87 ^c	
CuBr	3.81 ^a	5.15 ^a	4.166 ^a	
	4.18 ^b	5.17 ^b	4.54 ^b	
	3.18 ^c	4.69 ^c	3.64 ^c	
CuI	3.17 ^a	4.61 ^a	3.504 ^a	
	3.66 ^b	4.98 ^b	4.02 ^b	
	2.34 ^c	3.99 ^c	2.81 ^c	
AgF	4.40 ^a	6.14 ^a	5.96 ^a	6.2
	4.53 ^b	6.09 ^b	6.04 ^b	
	3.28 ^c	5.74 ^c	5.31 ^c	
AgCl	2.43 ^a	5.95 ^a	4.67 ^a	5.7
	3.27 ^b	6.29 ^b	5.19 ^b	
	1.85 ^c	5.72 ^c	4.32 ^c	
AgBr	2.38 ^a	6.02 ^a	4.52 ^a	
	2.88 ^b	6.24 ^b	4.85 ^b	
	1.57 ^c	5.68 ^c	4.01 ^c	
AgI	1.45 ^a	5.63 ^a	3.68 ^a	
	2.14 ^b	5.95 ^b	4.19 ^b	
	0.377 ^c	5.14 ^c	3.02 ^c	

^aCalculated using Pauling's value of polarizability for halogen

^bCalculated using molecular state value of polarizability for halogen

^cCalculated using Coker's value of polarizability for halogen

calculated for the ground state of eight molecules. The molecular constants used in these calculations are the most recent one given by Huber and Herzberg (1979). The α_e and $\omega_e X_e$ values thus obtained are given in Tables 5 and 6

Table 5. Calculated values of ν_e for Cu and Ag monohalides (cm^{-1}).

Molecules	$\alpha_e \times 10^{-2}$ observed	$\alpha_e \times 10^{-2}$ from Rittner	$\alpha_e \times 10^{-2}$ from T-Rittner	$\alpha_e \times 10^{-2}$ from Ionic
CuF	3.129	3.454 ^a	3.212 ¹	3.429 ^a
		3.272 ^b	3.16 ^b	3.424 ^b
		3.281 ^c	3.082 ^c	3.38 ^c
CuCl	0.996	1.065 ^a	1.037 ^a	1.240 ^a
		1.024 ^b	1.062 ^b	1.248 ^b
		0.979 ^c	1.023 ^c	1.284 ^c
CuBr	0.952	0.4408 ^a	0.4693 ^a	0.577 ^a
		0.467 ^b	0.477 ^b	0.581 ^b
		0.489 ^c	0.498 ^c	0.575 ^c
CuI	0.283	0.2841 ^a	0.2929 ^a	0.378 ^a
		0.289 ^b	0.298 ^b	0.380 ^b
		0.277 ^c	0.287 ^c	0.376 ^c
AgF	1.9206	1.791 ^a	1.965 ^a	1.998 ^a
		1.870 ^b	1.89 ^b	2.078 ^b
		1.771 ^c	1.912 ^c	1.967 ^c
AgCl	0.595	0.6035 ^a	0.6041 ^a	0.686 ^a
		0.541 ^b	0.615 ^b	0.692 ^b
		0.554 ^c	0.597 ^c	0.684 ^c
AgBr	0.228	0.2311 ^a	0.2475 ^a	0.2757 ^a
		0.235 ^b	0.2505 ^b	0.277 ^b
		0.226 ^c	0.2438 ^c	0.274 ^c
AgI	0.1413	0.1401 ^a	0.1495 ^a	0.1731 ^a
		0.146 ^b	0.1517 ^b	0.174 ^b
		0.136 ^c	0.146 ^c	0.173 ^c

^aCalculated from Pauling's value of polarizability for halogen

^bCalculated from molecular state value of polarizability for halogen

^cCalculated from Coker's value of polarizability for halogen

respectively. We have also evaluated the dipole moment for these molecules using the three models.

For ionic model, the charge shift Δr could be evaluated by iteration procedure which is then used to calculate the dipole moment. The dipole moments obtained by the three methods for three polarizability values are given in Table 4.

Table 6. Calculated values of $\omega_e x_e$ for Cu and Ag monohalides.

Molecules	$\omega_e x_e$ (cm ⁻¹) observed	$\omega_e x_e$ (cm ⁻¹) from Rittner	$\omega_e x_e$ (cm ⁻¹) from T-Rittner	$\omega_e x_e$ (cm ⁻¹) from Ionic
CuF	3.95	4.26 ^a	3.80 ^a	4.066 ^a
		3.99 ^b	3.55 ^b	4.040 ^b
		4.049 ^c	3.613 ^c	3.99 ^c
CuCl	1.58	1.924 ^a	1.803 ^a	2.151 ^a
		1.79 ^b	1.85 ^b	2.17 ^b
		1.692 ^c	1.774 ^c	2.26 ^c
CuBr	0.96	1.056 ^a	1.072 ^a	1.376 ^a
		1.095 ^b	1.150 ^b	1.388 ^b
		1.319 ^c	1.32 ^c	1.36 ^c
CuI	0.60	0.775 ^a	0.789 ^a	1.084 ^a
		0.790 ^b	0.806 ^b	1.089 ^b
		0.757 ^c	0.771 ^c	1.073 ^c
AgF	2.593	2.525 ^a	2.799 ^a	2.792 ^a
		2.730 ^b	2.65 ^b	2.988 ^b
		2.624 ^c	2.717 ^c	2.745 ^c
AgCl	1.17	1.394 ^a	1.238 ^a	1.495 ^a
		1.275 ^b	1.26 ^b	1.502 ^b
		1.208 ^c	1.217 ^c	1.48 ^c
AgBr	0.679	0.705 ^a	0.733 ^a	0.826 ^a
		0.533 ^b	0.743 ^b	0.830 ^b
		0.691 ^c	0.720 ^c	0.817 ^c
AgI	0.445	0.506 ^a	0.524 ^a	0.692 ^a
		0.533 ^b	0.533 ^b	0.691 ^b
		0.493 ^c	0.513 ^c	0.679 ^c

^a Calculated with Pauling's value of polarizability for halogen

^b Calculated with molecular state value of polarizability for halogen

^c Calculated with Coker's value of polarizability for halogen

4. Results and discussion

The molecular polarizability data given in Table 1 have been evaluated by the method suggested by Sangachin and Shanker (1989) and Kumar et al (1986). As is clear from Table 2 that $r^0/4\alpha_1\alpha_2$ values for the eight molecules considered here, lie in between 5-16 which are very different from those for alkali halides (of the order of 50). For copper halides, this value decreases very slowly; however, for silver halides this decrease is very rapid as we go from F to I. As expected the charge-shift for silver halides is nearly three times that of the copper halides. The repulsive parameter ρ evaluated for these polarizability values using the three potentials, remains nearly the same although the TR value is slightly

larger. However, it increases as we go from CuF to CuI or AgF to AgI. The change of metal ion charges ρ value in the same proportion as for the halogen ions. Though several methods are known to evaluate Van der Waals constant C , we estimated it using the simple London relation. The C is largest for Coker's polarizability value and smallest for molecular polarizability values. It also increases as we go from CuF to CuI or AgF to AgI.

The dipole moments for the eight molecules evaluated for the three polarizability values using Rittner, T-Rittner and ionic models are given in Table 4. The experimental values are known only for CuF, AgF and AgCl and they are compared in the same table. One can see from this table that Rittner method underestimates the dipole moment value while the other two methods are equally good and give better value. The Coker's polarizability value in the ionic model gives a slightly smaller value for μ but in TR model it is of right order. In the TR model μ changes very slowly as we go from CuF to CuI or AgF to AgI whereas for ionic model it changes much rapidly. The experimental value for other halides will justify the validity of the two model. In this study TR model seems to be better than the ionic model.

It is interesting to note that the ionic model for alkaline earths monohalides give an increasing value of μ as we go from fluorides to iodides exactly in accordance with the experimental observation. The same model however for these molecules, gives a decreasing value of μ as we go from CuF/AgF to CuI/AgI. The experimental value known for AgF to AgCl shows a similar trend. The vibration-rotation interaction constant κ_0 and the harmonic constant calculated using three models and three polarizability values for these molecules are given in Tables 5 and 6. The ionic model over-estimates the molecular parameters for all the three polarizability values. The Rittner and T-Rittner models predict the two constants equally good for all the three polarizability values. However, the values obtained using molecular polarizability and Coker's values of polarizability are definitely better than for Pauling's values. Here also, the TR model seems to give better value than other two models.

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