

AN APPRAISAL OF THE MOLECULAR MODEL FOR THE V_k CENTRE

P. W. TASKER and A. M. STONEHAM

Theoretical Physics Division, AERE, Harwell, Oxon OX11 0RA, England

(Received 13 October 1976; accepted 25 February 1977)

Abstract—The V_k centre in halide crystals is often described in terms of an X_2^- molecule ion. Recent molecular calculations for the halogen molecule negative ions have enabled a detailed comparison to be made between the theoretical anion and the results from optical and spin resonance studies on the crystals. The optical absorption line widths are naturally dependant on the host lattice, but the excitation energies and spin resonance constants may be readily interpreted in terms of the molecule. Certain anomalies in the spin resonance data for the heteronuclear defects, in particular ClI^- and BrI^- , show that the simple wavefunction constructed from “s” and “p” atomic orbitals does not adequately describe the polarisation of the large halogen atoms, and a more flexible wavefunction will be needed to calculate the spin resonance constants for these ions.

1. INTRODUCTION

The self trapped hole in ionic halide crystals has been observed by optical and spin resonance spectroscopy and the experiments are usually interpreted in terms of a defect molecule [1-12]. The observed energy levels resemble those of the halogen molecule negative ions (X_2^-) and thus the stabilisation of the hole comes from the molecular binding energy.

Recent valence bond calculations [13] on the heavier molecular ions, including the mixed halogen molecules, permit a detailed comparison between experiment and theory. The excitation energies obtained by calculation should be directly comparable with experiment, the vibrational frequencies give a sensitive test of the influence of the host lattice and the detailed spin resonance measurements provide unique information on the wave function of the defect.

2. EXCITATION ENERGIES

The electronic ground state of the X_2^- ion is a $^2\Sigma_u^+$ and in terms of molecular orbitals the valence electron configuration can be written as $(\sigma_g)^2(\pi_u)^4(\pi_g)^4(\sigma_u)^1$. The electronically excited states derived by transferring the hole to the lower molecular orbitals are $^2\Pi_g$, $^2\Pi_u$ and $^2\Sigma_g^+$. The transitions to the $^2\Pi_g$ and $^2\Sigma_g^+$ stages are observed in the IR and UV spectrum respectively and the transition energy to the $^2\Pi_u$ state is deduced from spin resonance studies since the spin-orbit interaction will couple the $^2\Sigma_u^+$ and $^2\Pi_u$ states. The spin orbit interaction will also split the $^2\Pi$ states into two components and this effect becomes increasingly important for the heavier halogens.

Figure 1 shows the excitations as a function of internuclear distance for the halogen molecule ions, as calculated by the valence bond method [13]. Also shown are the experimental results for a variety of crystals [1-12] and for I_2^- in solution [14]. If the molecular model of the V_k centre provides a good description of the defect, the three excitation energies should correspond to a single internuclear separation, and deviation of this separation from the molecular equilibrium bond length gives a measure of the influence of the crystal on the

defect. The internuclear separation may naturally vary slightly from crystal to crystal.

With the exception of certain spin resonance results, the measurements agree to a single internuclear separation to within 5%. However, the calculations [13] did not include the spin-orbit interaction which will split the $^2\Pi_u$ and $^2\Pi_g$ states. The observed IR excitation corresponds to the transition $^2\Pi_{1/2g} \leftarrow ^2\Sigma_u^+$ which is more intense for the heavier halogens than the transition to the $^2\Pi_{3/2g}$ state since it is able to “borrow” intensity from the σ polarised transition through the spin-orbit coupling of $^2\Pi_{1/2g}$ with the $^2\Sigma_u^+$ state [12]. The calculated energy is for the average of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states and so the experimental points should be plotted above the calculated curve and hence at larger internuclear distances. This effect is negligible for Cl_2^- , but for Br_2^- a second weaker absorption has been observed in KBr at 1.38 eV and for I_2^- in KI at 1.08 eV [12] and in solution at 1.21 eV [14]. These excitations correspond to the $^2\Pi_{3/2g} \leftarrow ^2\Sigma_u^+$ transition, and if one takes the average of the two transition energies, and plots that on the theoretical curve bond lengths still agree to within 5%.

At large internuclear separations, the $^2\Pi_u$ states are expected to show a larger splitting than the $^2\Pi_g$ states since they correlate with different atomic states [13]. The ground $^2\Sigma_u^+$ state will be coupled by the spin-orbit interaction with the $^2\Pi_{1/2u}$ component, but in the presence of a lower symmetry, crystal field the spin resonance studies can give an estimate of the transition energy to the average of the $^2\Pi_u$ electronic states [11], and should therefore agree with the calculation. The results for Br_2^- in sodium bromide and the I_2^- results are low compared with the optical measurements, but the deduction of the excitation energy from the spin resonance g -factors relies on several approximations which may not be valid, particularly in the case of the heavier halogens. These approximations will be considered in greater detail in Section 4.

Average bond lengths for X_2^- in a crystal, derived from the spectroscopic data, are 5.3, 5.7 and 6.3 bohr for Cl_2^- , Br_2^- and I_2^- respectively, compared with 5.1, 5.5

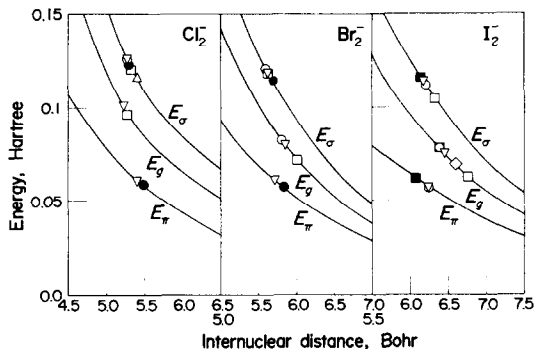


Fig. 1. Calculated excitation energies as a function of internuclear distance for Cl_2^- , Br_2^- , I_2^- . Transitions are labelled $E_g(^2\Pi_g \leftarrow ^2\Sigma_u^+)$, $E_g(^2\Pi_u \leftarrow ^2\Sigma_u^+)$, $E_g(^2\Sigma_g^+ \leftarrow ^2\Sigma_u^+)$. Experimental results for the V_k centre in a variety of host lattices are also shown. Δ , Li; \square , Na; ∇ , K; \circ , Rb; \diamond , Cs; \bullet , NH_4 ; \blacksquare , I_2^- soln.

and 6.2 bohr calculated for the free molecules[13], although a more detailed interpretation of the spin resonance data leads to shorter bond lengths[20]. The crystal appears to have only a small effect on the molecular defect and the description of the excitation energies in terms of the molecular states is a good approximation. This is in agreement with the conclusion drawn previously for the fluorides[15].

Figure 2 shows the excitation energy curves for the mixed halogen molecules (XY^-) for comparison although there are insufficient experimental data for a similar analysis.

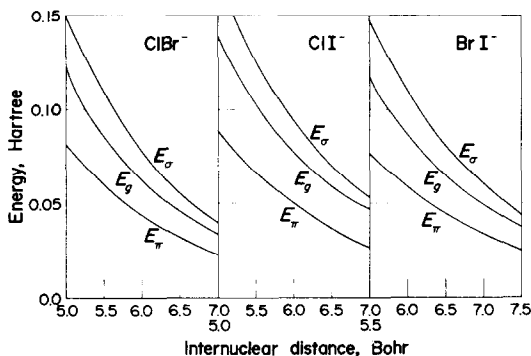


Fig. 2. Calculated excitation energies as a function of internuclear distance for ClBr^- , ClI^- , BrI^- . Transitions are labelled as in Fig. 1, but g, u symmetry no longer applies.

3. LINE WIDTHS

Table 1 shows the widths of the observed optical absorption lines. The line widths depend on the shape of the ground and excited state potential curves and can be approximated by[16]

$$W = 27A(\mu k)^{-1/4} \text{ eV}$$

where A is the gradient of excited state curve, and μ and k are the effective mass and force constant for the defect in its ground state. All energies are expressed in Rydbergs, distances in bohr and mass in units of the electron mass. The calculated widths are also shown in

Table 1; the force constants obtained from the fitting of the ground state potential curves have been used[13].

The experimentally observed lines are considerably broader than those calculated, with the widths decreasing with increasing cation size. Two mechanisms provide possible interpretations of the line broadening. Firstly, the electronically excited state may interact with the valence band of the crystal causing delocalisation of the hole. This will lower the excited state energy and increase the slope of the excitation energy curve, and thus broaden the absorption band[16]. However, a large change in slope is required to account for the line broadening, and this would considerably worsen the agreement with the excitation energies.

The force constant for the vibration is also affected by the ability of the lattice ions to follow the motion of the vibrating V_k ions, and a lower force constant will give a broader observed optical line. As the relative cation mass increases the lattice ions will become less able to follow the V_k vibration adiabatically leading to an increase in effective force constant and a narrowing of the line.

The results show the sensitivity of the line width to the environment of the host lattice. The widths for I_2^- in solution were estimated from the figure in Ref. [14], and reflect the weaker effect of the environment in solution.

4. ELECTRON SPIN RESONANCE

The electron spin resonance measurements provide the most detailed information about the defect wavefunction. If the defect is primarily a halogen molecule negative ion and only slightly perturbed by the lattice, the wavefunction should show axial symmetry and this will be reflected in the measurements of the g -factors and hyperfine splittings. The data are summarised in Tables 2 and 3, and show that the two measurements perpendicular to the defect internuclear axis are very close, or equal, deviating most substantially for ClI^- and BrI^- , whereas the measurement along the axis gives a different value in accordance with the molecular symmetry.

The ground electronic state of the X_2^- molecule is $^2\Sigma_u^+$ with zero orbital angular momentum about the internuclear axis. Consequently any deviation in the g -factors from the free electron value of 2.0023 is due to spin-orbit coupling to states of higher angular momentum. The $^2\Pi_u$ state is the only low-lying, excited state that will couple with the ground state, and gives to first order in λ/E [1-3, 11, 17, 18]

$$\Delta g_x = \Delta g_y = \alpha_p^2 \cdot 2\lambda/E_g$$

where E_g is the $^2\Pi_u \leftarrow ^2\Sigma_u^+$ excitation energy and λ is the spin-orbit coupling parameter when the interaction can be approximated by $\lambda L \cdot S$. The wavefunction of the hole is often approximated as $\gamma_1\psi_1 + \gamma_2\psi_2$, ψ_1 and ψ_2 being atomic wavefunctions written as $\psi = \alpha_s|s\rangle + \alpha_p|p\rangle$. For a homonuclear molecule $\gamma_1 = \gamma_2$. Overlap is usually neglected in the normalisation of this wavefunction, giving $\gamma_1^2 + \gamma_2^2 = 1$ and $\alpha_s^2 + \alpha_p^2 = 1$, where α_p^2 is then associated with the fractional "p" character of the bonding. This neglect of overlap can lead to significant errors in the determination of the matrix elements and hence in the

Table 1. Experimental line widths for the optical absorption of V_k centres[3, 6-8] and for I_2^- in rigid solution[14] compared with calculated values for the molecule ions[13]

Crystal and defect	UV transition		IR transition	
	Experimental line width (eV)	Calculated line width (eV)	Experimental line width (eV)	Calculated line width (eV)
LiCl(Cl ₂ ⁻)	1.47	0.591	—	0.248
NaCl(Cl ₂ ⁻)	1.11		—	
KCl(Cl ₂ ⁻)	0.81		0.37	
RbCl(Cl ₂ ⁻)	0.76		—	
NH ₄ Cl(Cl ₂ ⁻)	0.83-1.0	0.475	0.37	0.212
KBr(Br ₂ ⁻)	0.73		0.26	
NH ₄ Br(Br ₂ ⁻)	0.80	0.372	0.27	0.156
KI(I ₂ ⁻)	0.55		0.22, 0.19	
I ₂ ⁻ soln.	~0.40	0.570	~0.21	0.322
BrCl ⁻ (in KCl)	0.76		0.30	
ICl ⁻ (in KCl)	0.60	0.452	0.23	0.211
BrI ⁻	—	0.424	—	0.200

Table 2. Hyperfine constants for Cl, Br and I in homonuclear and heteronuclear XY⁻ defects[4-11]. α_s^2 is the "s" character of the wavefunction (see text)

Atom	Constants	X ₂ ⁻	ClBr ⁻	ClI ⁻	BrI ⁻
¹²⁷ I	A_{11}	385-398		394.5	408.2
	A_{\perp}	140-147		283	229
	A_{\pm}			316	358
	a	213		331	332
	b	83		31	38
	α_s^2	0.026		0.099	0.083
⁸¹ Br	A_{11}	450.5	484.6		52
	A_{\perp}	81	115.5	—	small
	A_{\pm}				
	a	204	238		~20
	b	123	123		~17
	α_s^2	0.017	0.020		~0.01
³⁵ Cl	A_{11}	101.3	89.6	61.2	
	A_{\perp}	12.6	7.5	<4	—
	A_{\pm}				
	a	42	35	22	
	b	29	27	30	
	α_s^2	0.015	0.013	0.007	

calculation of E_g [11]. Calculations are usually taken to at least second order in λ/E , when Δg_z becomes different from zero.

In the fourth column of Table 3 the values of $g_x + g_y - 2g_z$ are tabulated, and these should be approximately equal to $\alpha_p^2 4\lambda/E_g$ for the homonuclear molecules. As the spin-orbit interaction can usually be approximated as a sum of terms for each nucleus, the same Δg value for the heteronuclear molecules should be equal to $4(\alpha_{p1}^2 \gamma_1^2 \lambda_1 + \alpha_{p2}^2 \gamma_2^2 \lambda_2)/E_g$. The data for most of the heteronuclear defects can be understood in this simple way. Data for the fluorine defects have been included in Table 3 for comparison. Clearly the Δg values for the heteronuclear defects are greater than the unweighted

Table 3. g -Factors for the V_k centre defects[1-11]. The Δg values for the heteronuclear centres are compared with the average Δg for the corresponding homonuclear centres

Defect	g_z	g_x	g_y	$\Delta g = g_x + g_y - 2g_z$	Average for Δg for $(X_2^- + Y_2^-)/2$
F ₂ ⁻	2.0020	2.0218	2.0218	0.0396	
Cl ₂ ⁻	2.0014	2.0444	2.0423	0.0839	
Br ₂ ⁻	1.9830	2.169	2.164	0.367	
I ₂ ⁻	1.9118	2.27	2.27	0.7164	
FCI ⁻	2.0018	2.030	2.030	0.0564	0.0618
FBr ⁻	1.9891	2.125	2.125	0.2718	0.2033
FI ⁻	1.9363	2.26	2.26	0.6474	0.378
ClBr ⁻	1.9840	2.133	2.135	0.300	0.255
ClI ⁻	1.855	2.326	2.395	1.008	0.400
BrI ⁻	1.9041				

mean of the values for homonuclear defects, since the density of the unpaired electron is greatest on the least electronegative atom. The Δg for the heteronuclear defect is closer to the results for the heavier halogen ion than the lighter one.

The results for ClI⁻ cannot be so easily explained, for the Δg for this defect is greater than that for I₂⁻. With the simple model presented here this can only be understood if the heteronuclear wavefunction shows much greater "p" character than the homonuclear wavefunction. For heteronuclear molecules the wavefunction no longer has gerade, ungerade parity and so the lowest-lying ²Π state may also be coupled to the ground ²Σ state. This will lead to an increase in Δg , but, since this second term in the expression for Δg is zero for the homonuclear defects, it is expected to be small for the XY⁻ centres [5]. In any case, neither of the interpretations given above are consistent with the data from the hyperfine splittings.

The hyperfine constants are given in Table 2 as well as

two constants a and b calculated from

$$a = (A_{11} + 2A_{12})/3$$

$$b = (A_{11} - A_{12})/3.$$

These are related to the simple wavefunction by [1-3, 17, 18]

$$a = \gamma^2 \alpha_s^2 \frac{16}{3} \pi g_N \beta_N \beta |s(0)|^2$$

$$b = \gamma^2 \alpha_p^2 \frac{4}{15} g_N \beta_N \beta \langle r^{-3} \rangle$$

and are directly proportional to the fractional "s" and "p" characters of the wavefunction, if we neglect the overlap. (The subscript N refers to the nuclear constants). The values of $\langle r^{-3} \rangle$ and $|s(0)|^2$ vary along the homologous series of halogens but the ratio $\langle r^{-3} \rangle / |s(0)|^2$ is approximately constant and taken as 0.65 [5]. The calculated values of α_s^2 are shown in Table 2 and, although the neglect of overlap may make these fractions smaller than they should be, the trend is clear. The proportion of "s" character on the heavier atom in the heteronuclear defect is greater than in the corresponding homonuclear defect and the effect is most marked for the most disparate size of atoms. This agrees with the valence bond calculation [13] in which the wavefunction changed in the same way. This can be easily understood in terms of the polarisation of the larger atom by the charge accumulated on the smaller one, which leads to hybridisation of the orbitals on the larger atom. However it is the opposite to the change required to interpret the g -factors for ClI^- .

We can check the consistency of our argument by calculating the ratio of the constant a or b for the same atom in a homonuclear or heteronuclear defect. This gives us the increase (or decrease) in "s" or "p" character of the atomic wavefunction. The calculated α_s^2 and α_p^2 for the homonuclear molecules can be used to calculate the α_s^2 and α_p^2 for the atom in the heteronuclear molecule, except that the atomic functions will no longer be normalised, i.e. $\alpha_s^2 + \alpha_p^2 \neq 1$, for the atom in the heteronuclear molecule since the hole density is not equally divided between its atoms. The lighter atom may be expected to show a net decrease in $\alpha_s^2 + \alpha_p^2$ but this should be compensated by a net increase in hole density on the heavier atom. Thus for a heteronuclear defect XY^- ,

$$\frac{1}{2}(\alpha_s^2 + \alpha_p^2)_x + \frac{1}{2}(\alpha_s^2 + \alpha_p^2)_y = 1.0.$$

It should be noted that since we are concerned with the ratios of a and b , this argument is not dependent on the values chosen for $\langle r^{-3} \rangle$ and $|s(0)|^2$, and the effect of the neglect of overlap is minimised as we are comparing the wavefunctions for the homonuclear and heteronuclear defects, calculated in the same way.

The evaluation of the sum for ClBr^- gives a total of 0.966 which is very close to the theoretical value of 1.0,

but the values for BrI^- and ClI^- are 0.312 and 0.716 respectively. If the wavefunction for the hole in a homonuclear molecule can be described only in terms of "s" and "p" orbitals, this is no longer adequate as a description of BrI^- and ClI^- , unless the "s" and "p" orbitals of I in BrI^- and ClI^- are strongly affected by the heteronuclear partner. Since the equilibrium interatomic spacings in the heteronuclear molecules obey an additivity rule [13], simple changes in the radial parts of the "s" and "p" functions are unlikely to be the main explanation. The simplest interpretation is that a calculation of the bonding in terms of just "s" and "p" atomic orbitals is not capable of describing the polarisation of the large atom, that may be due to the unequal charge distribution or the crystal field. The wavefunction can be made more flexible by inclusion in the basis of higher angular momentum orbitals such as the atomic "d" orbitals, which for the heavier halogens are not too far removed in energy from the valence "s" and "p" orbitals. Clearly if the hole density near an atomic nucleus lies partly in higher angular momentum orbitals this will affect the spin resonance constants, and provides not only a consistent description of the anisotropic hyperfine constants but also gives an explanation for the large deviation in g -factor for the heteronuclear molecules. The iodine-containing molecules even show a large shift in the g_z component which should be close to the free electron value. These conclusions are in agreement with the work of Jette and Adrian who have calculated anisotropic hyperfine constants using a valence bond wavefunction constructed from "s" and "p" atomic orbitals [19]. They found that the agreement between theory and experiment was poorest for the heaviest halogen in a heteronuclear XY^- molecule, and the discrepancy increased with the dissimilarity of the two halogens.

5. CONCLUSIONS

We have compared the principal, experimental data on the V_k centre with calculations for the X_2^- molecule ion. The widths of the optical absorption lines are clearly very dependant on the relaxation of the crystal and one would not expect them to resemble the calculated values. However, they do approach the molecular values as the cation mass increases, and for I_2^- in solution where the environmental effects are weaker. The absorption energies agree very well with the calculated X_2^- excitations and suggest that the molecular model describes the V_k centre well, with only very small deviations in geometry induced by the lattice environment. The axial symmetry of the spin resonance data also agrees with the molecular model, but the simple molecular wavefunction is inadequate in explaining the results for the heteronuclear ions. This is due to the polarisation of the larger ion but may, nevertheless, be a molecular effect rather than a lattice effect, since the anomaly arises for heteronuclear defects. However the lattice has some influence since the heavy ions also show the largest deviations from axial symmetry. Considering the large polarisability of the heavy halogens, it is not surprising that both its atomic partner and the crystal lattice should affect the wave-

function. The excitation energies are still well described by calculations based on a more restricted wavefunction, since a first order change affects the energy only in second order. These results show the extreme sensitivity of the spin resonance measurements as a means of probing the wavefunction.

REFERENCES

1. Silsbee R. H., In *Electron Paramagnetic Resonance* (Edited by S. Gerschwind). Plenum Press, New York (1972).
2. Stoneham A. M., *Theory of Defects in Solids*. Clarendon Press, Oxford (1975).
3. Kabler, M. N., In *Point Defects in Solids* (Edited by J. H. Crawford and L. M. Slifkin), Vol. 1. Plenum Press, New York (1972).
4. Wilkins J. W. and Gabriel J. R., *Phys. Rev.* **132**, 950 (1963).
5. Schoemaker D., *Phys. Rev.* **149**, 693 (1966).
6. Delbecq C. J., Schoemaker D. and Yuster P. H., *Phys. Rev.* **B7**, 3933 (1973).
7. Delbecq C. J., Schoemaker D. and Yuster P. H., *Phys. Rev.* **B3**, 473 (1971).
8. Goldberg L. S. and Meistrich M. L., *Phys. Rev.* **172**, 877 (1968).
9. Schoemaker D., *Phys. Rev.* **174**, 1060 (1968).
10. Dreybrodt W. and Stilber D., *Phys. Status Solidi* **16**, 215 (1966).
11. Schoemaker D., *Phys. Rev.* **B7**, 786 (1973).
12. Delbecq C. J., Hayes W. and Yuster P. H., *Phys. Rev.* **121**, 1043 (1961).
13. Tasker P. W., Balint-Kurti G. G. and Dixon R. N., *Mol. Phys.* **32**, 1651 (1976).
14. Shida T., Takahashi Y., Hatano H. and Imamura M., *Chem. Phys. Letters* **33**, 491 (1975).
15. Norgett M. J. and Stoneham A. M., *J. Phys.* **C6**, 229 (1973).
16. Jette A. N., Gilbert T. L. and Das T. P., *Phys. Rev.* **184**, 884 (1969).
17. Castner T. G. and Känzig W., *J. Phys. Chem. Solids* **3**, 178 (1957).
18. Slichter C. P., *Principles of Magnetic Resonance*. Harper & Row, New York (1963).
19. Jette A. N. and Adrian F. J., *Phys. Rev.* **B14**, 3672 (1976).
20. Lagendijk A. and Schoemaker D., *Phys. Rev.* **B11**, 4030 (1975).