

Charge Transfer Model for Alkali Halide Electronic Transition Strengths

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A simple one-electron charge transfer model due to Mulliken is applied to alkali halide molecules to estimate the relative amount of parallel and perpendicular character in the "bundles" of unresolved electronic transitions which lead to dissociation and produce a normal or an excited alkali atom. If the bonding in the ground state is "purely ionic" and that in the excited state is "purely atomic," the model indicates that most of the intensity will appear in perpendicular transitions. If the ionic and atomic character are mixed equally, however, the parallel transitions pre-empt all of the intensity, just as with purely covalent bonding. Even a slight amount of mixing ($\sim 5\%$) is sufficient to put comparable intensity into the parallel and perpendicular transitions, in agreement with the scanty experimental evidence available. Numerical calculations are presented for the LiF molecule.

INTRODUCTION

In photodissociation of a diatomic molecule, the primary factor which determines the form of the angular distribution of products and the shape of the atomic fluorescence line if an excited atom is produced is just the relative importance of *parallel* (e.g., $\Sigma \rightarrow \Sigma$) and *perpendicular* (e.g., $\Sigma \rightarrow \Pi$) character in the electronic transition (1, 2). If either the parallel or the perpendicular component is predominant, the product distribution is expected to show a marked anisotropy and several experiments, reviewed in Ref. 1, have been proposed which intend to exploit this possible anisotropy. The alkali halides are usually considered as prototype molecules for these photodissociation experiments.

There is some evidence concerning the relative contribution of parallel and perpendicular transitions in the photodissociation of NaI. Mulliken has discussed the dissociation into a normal sodium atom and a normal or metastable iodine atom (3). His analysis of the spectra (in contrast to his theoretical expectation), indicated that the parallel and perpendicular transitions which produce a normal sodium atom are probably of comparable intensity. Likewise, Mitchell's evidence for an isotropic angular distribution of photodissociation products (2, 4) and Hanson's observation of identical Doppler broadening for the sodium D fluores-

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cence doublets (2, 5) suggest that this also holds for the transitions which produce an excited sodium atom. This is all rather circumstantial evidence, however.

As yet only a few theoretical calculations of electronic transition dipole moments have been attempted (6, 7), and it appears that no numerical estimates have been made for alkali halide transitions. In an extensive study of the one-electron molecules H_2^+ and HeH^{++} , Bates and coworkers (6) have compared results obtained from the exact (fixed nuclei) wavefunctions with those from various LCAO approximations, and find that the LCAO results are often seriously in error. Since for other molecules the transition dipole is not a one-electron operator it remains a recalcitrant property even for Hartree-Fock calculations, although promising results have recently been obtained for H_2 (7).

In order to examine the qualitative features which govern the relative intensity of parallel and perpendicular transitions, we have considered a simple charge transfer model for transitions to the manifold of repulsive states which lead to the dissociation of alkali halide molecules and produce normal ($^2S_{1/2}$) or excited ($^2P_{1/2}$, $^2P_{3/2}$) alkali atoms. This treatment, of course, may be a woefully inadequate approximation, but as a reference model it is so simple that the results derived from it have some interest in their own right, especially since they seem to contradict "intuition." Thus, for an ionic molecule a charge transfer model might be expected to favor strong parallel transitions in which the electron would oscillate along the internuclear axis in resonance with the exciting light. However, the qualitative analysis and numerical calculations for the LiF molecule show that as the ionic character of the molecular bonding increases, the model puts more and more of the intensity into perpendicular rather than parallel transitions.

CHARGE TRANSFER MODEL

The ground electronic state of an alkali halide has an ionic structure, M^+X^- , and since the molecule dissociates into atoms rather than ions, the pumping transition transfers an electron from X^- to M^+ . We ignore all other electrons, and assume the valence electron which "jumps" goes from a p atomic orbital on the halogen to either an s or p orbital on the alkali atom.

In general terms, the model assumes the wave functions for the initial and final states are separable as

$$\psi_i = \phi_i(\text{electrons 1, 2}) \phi(\text{others}),$$

$$\psi_f = \phi_f(\text{electrons 1, 2}) \phi(\text{others}),$$

where ϕ_i and ϕ_f are orthogonal functions made up of one-electron orbitals for electrons 1 and 2, the electrons which in the initial state occupy the halogen p orbital. Although the interaction of 1 and 2 is neglected, they must be considered together, as either may make the jump. For this model the electronic transition

dipole moment (\mathcal{S}) is therefore given by

$$\mathbf{u}_{if} = e \int \phi_i^*(\mathbf{r}_1 + \mathbf{r}_2) \phi_f d\tau_1 d\tau_2, \quad (1)$$

where \mathbf{r} is the coordinate vector (with components x, y, z) of the jumping electron. The wave functions are formed from atomic orbitals ϕ_A on the alkali atom and ϕ_B on the halogen, and we take

$$\begin{aligned} \phi_i &= N_i \{ \phi_B(1)\phi_B(2) + \alpha 2^{-1/2} [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \}, \\ \phi_f &= N_f \{ 2^{-1/2} [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] - \beta \phi_B(1)\phi_B(2) \}. \end{aligned} \quad (2)$$

In ϕ_i the leading term puts both valence electrons on the B atom (ionic bonding) and in ϕ_f it puts one or the other on the A atom (atomic bonding). The terms in α and β allow arbitrary mixing of these descriptions. The coefficients α and β are related by the requirement that ϕ_i and ϕ_f be orthogonal, and N_i and N_f are normalization factors. Thus we have

$$\begin{aligned} \alpha &= (\beta - S)/(1 - \beta S + \frac{1}{2}S^2), \\ N_i &= (1 + 2\alpha S + \alpha^2 + \frac{1}{2}\alpha^2 S^2)^{-1/2}, \\ N_f &= (1 - 2\beta S + \beta^2 + \frac{1}{2}\beta^2 S^2)^{-1/2}, \end{aligned} \quad (3)$$

where

$$S = 2^{1/2} \langle \phi_A | \phi_B \rangle$$

measures the overlap of the atomic orbitals.

According to Eqs. (1) and (2) the transition dipole moment is

$$\mathbf{u}_{if} = e N_i N_f [\alpha \langle \mathbf{r} \rangle_A - \alpha S \mathbf{D} + (1 - \alpha\beta) \mathbf{D}], \quad (4)$$

where

$$\langle \mathbf{r} \rangle_A = \langle \phi_A | \mathbf{r} | \phi_A \rangle$$

and

$$\mathbf{D} = 2^{1/2} \langle \phi_A | \mathbf{r} | \phi_B \rangle.$$

Since ϕ_i and ϕ_f are orthogonal, \mathbf{u}_{if} does not depend on the choice of the coordinate system (\mathcal{S}). To simplify Eq. (4), we have put the origin on the B atom (the halogen) and the z -axis through the A atom (the alkali atom); therefore

$$\langle x \rangle_A = \langle y \rangle_A = 0$$

and

$$\langle z \rangle_A = r_0, \text{ the bond distance.}$$

Also, the overlap S vanishes unless ϕ_A and ϕ_B have the same symmetry with

respect to the molecular axis. Hence in Eq. (4) the leading term in r_0 and that involving SD contribute only to the *parallel* transitions ($\mu_{\parallel} = \mu_z$) and only the final term involving $(1 - \alpha\beta)D$ contributes to the *perpendicular* transitions ($\mu_{\perp} = \mu_x = \mu_y$).

As set up in Eq. (2), the present model does not possess a "purely covalent" limit appropriate to a homopolar molecule. However, an equal mixture of the ionic and atomic terms ($\alpha = \beta = 1$) yields

$$\mu_{\parallel}(\alpha = \beta = 1) \simeq \frac{1}{2}(er_0 - SD)/(1 - \frac{1}{2}S^2)^{1/2}, \quad (5a)$$

$$\mu_{\perp}(\alpha = \beta = 1) = 0. \quad (5b)$$

This result is identical (except for the small term SD) to the formula derived by Mulliken (8) for the prototype charge transfer transition $\sigma_g 1s \rightarrow \sigma_u 1s$ in H_2^+ . If r_0 is not too small, the overlap S may be neglected, and the transition moment is roughly equal to the dipole moment of an electron oscillating parallel to the molecular axis with an amplitude $\frac{1}{2}r_0$; there is no intensity in perpendicular transitions.

If the initial state is almost "purely ionic" ($\alpha \ll 1$) and the final state almost "purely atomic" ($\beta \ll 1$) we have

$$\mu_{\parallel}(\alpha \ll 1, \beta \ll 1) \simeq \alpha er_0 + 2^{1/2}\langle \phi_A | z | \phi_B \rangle, \quad (6a)$$

$$\mu_{\perp}(\alpha \ll 1, \beta \ll 1) \simeq 2^{1/2}\langle \phi_A | x | \phi_B \rangle = 2^{1/2}\langle \phi_A | y | \phi_B \rangle. \quad (6b)$$

Since the term αer_0 in μ_{\parallel} is quite small in this limit, the relative importance of parallel and perpendicular transitions depends primarily on the ratio of the two center dipole integrals

$$\langle \phi_A | z | \phi_B \rangle \quad \text{and} \quad \langle \phi_A | x | \phi_B \rangle.$$

The factors of $2^{1/2}$, which become factors of 2 in the transition intensity, appear because either of the valence electrons in ϕ_i can make the jump. For the alkali halide transitions of interest here, we expect the limiting case given in Eqs. (6) to be adequate, since as long as α and $\beta \gtrsim 0.5$ and $S \lesssim 0.10$ it is a close approximation to the general formula of Eq. (4).

EVALUATION OF DIPOLE INTEGRALS

If the photodissociation produces an excited alkali atom, ϕ_A is an np orbital, ϕ_B is an $n'p$ orbital and there are only four types of nonvanishing two-center dipole integrals:

$$\langle np_z | z | n'p_z \rangle, \quad (7a)$$

$$\langle np_x | z | n'p_x \rangle = \langle np_y | z | n'p_y \rangle, \quad (7b)$$

$$\langle np_x | x | n'p_x \rangle = \langle np_y | y | n'p_y \rangle, \quad (7c)$$

$$\langle np_z | x | n'p_x \rangle = \langle np_z | y | n'p_y \rangle. \quad (7d)$$

The integrals of type (a) and (b) correspond to parallel transitions, and those of type (c) and (d) to perpendicular transitions. The integrals of type (b) and (c) have the same value, since

$$z | n'p_x \rangle = x | n'p_z \rangle$$

for any n' . The factors $\langle np_x | z$ and $\langle np_z | x$ in the integrands of (b) and (d) are not the same, however, since the origin of the \mathbf{r} vector is on atom B . Thus for dissociation into excited alkali atoms we need to compare the magnitude of only three integrals:

$$\begin{aligned} I_{zz}^* &= \langle np_z | z | n'p_z \rangle, \\ I_{xz}^* &= \langle np_x | x | n'p_z \rangle, \\ I_{xx}^* &= \langle np_z | x | n'p_x \rangle. \end{aligned}$$

If the photodissociation produces a normal alkali atom ϕ_A is an ns orbital, and similarly we find there are only two types of nonvanishing dipole integrals:

$$\begin{aligned} I_{zz} &= \langle ns | z | n'p_z \rangle, \\ I_{xx} &= \langle ns | x | n'p_x \rangle. \end{aligned}$$

We shall use Slater's rules (9) for approximate atomic orbitals. For LiI' the principal quantum numbers are $n = n' = 2$ and the effective nuclear charges are $C_{Li} = 1.3$ and $C_F = 5.2$. Since the product of a component of \mathbf{r} and a Slater orbital is another Slater orbital with a different effective nuclear charge and normalization factor, the dipole integrals may be further reduced to two-center overlap integrals. For example,

$$z | 2p_z(C) \rangle = N' | 3d_{z^2}(C') \rangle$$

and

$$x | 2p_z(C) \rangle = z | 2p_x(C) \rangle = N' | 3d_{xz}(C') \rangle,$$

where C and C' are the effective nuclear charges in the Slater orbitals, with $C' = \frac{3}{2}C$, and N' is the ratio of normalization factors, $N' = N_{2p}(C)/N_{3d}(C') = 6^{1/2}/C$. Since r is measured from the F atom as origin, $C = C_F$ in these expressions. Three of the dipole integrals may now be rewritten as

$$I_{zz}^* = (6^{1/2}/C_F) \langle 2p_z(C_{Li}) | 3d_{z^2}(C_F') \rangle, \quad (8a)$$

$$I_{xz}^* = (6^{1/2}/C_F) \langle 2p_x(C_{Li}) | 3d_{xz}(C_F') \rangle, \quad (8b)$$

$$I_{zz} = (6^{1/2}/C_F) \langle 2s(C_{Li}) | 3d_{z^2}(C_F') \rangle. \quad (8c)$$

Since the x -coordinate of the electron is the same whether measured from the Li atom or the F atom, the I_{xx}^* integral may be evaluated in the same way as I_{xz}^* , but with $C = C_{Li}$; thus

$$I_{xx}^* = (6^{1/2}/C_{Li}) \langle 3d_{xz}(C'_{Li}) | 2p_x(C_F) \rangle. \quad (8d)$$

Finally, to reduce the I_{xx} integral, we use

$$\langle 2s(C) | x = N'' \langle 3p_x(C') | ,$$

where $N'' = N_{2s}(C)/N_{3p}(C') = 10^{1/2}/C$, and thus

$$I_{xx} = (10^{1/2}/C_{Li}) \langle 3p_x(C'_{Li}) | 2p_x(C_F) \rangle. \quad (8e)$$

These two-center overlap integrals can be evaluated by means of a standard IBM 7094 computer program (10).

RESULTS FOR LiF

The qualitative behavior of the dipole integrals is readily visualized, as illustrated in Figs. 1-3 and Table I for the LiF transitions which produce an excited Li atom. Thus, we see that

$$I_{xx}^* > I_{xz}^* \gg I_{zz}^* ,$$

since Figs. 1 and 2 show that (in the notation of Table I) the L and R factors overlap constructively in I_{xx}^* and I_{xz}^* whereas in Fig. 3 one lobe of the L factor completely surrounds the R factor and consequently extensive cancellation occurs in the integrand of I_{zz}^* . Similarly, for transitions which produce a normal Li atom, we expect that

$$I_{xx} \gg I_{zz} .$$

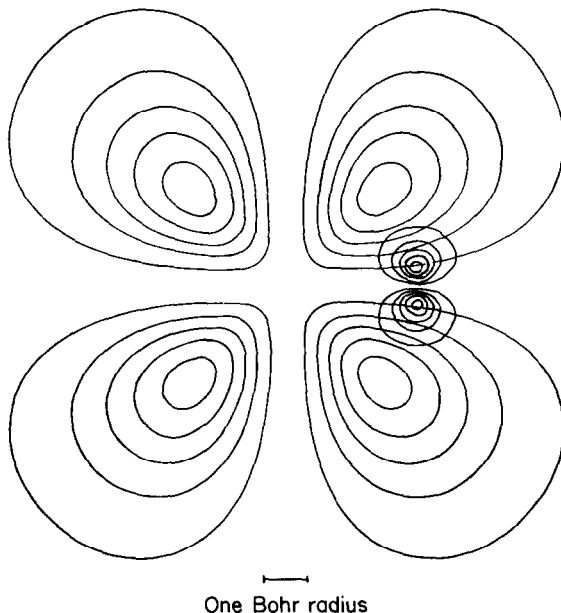


FIG. 1. Contour map of factors $\langle 2p_z(\text{Li}) | x$ and $| 2p_x(\text{F}) \rangle$ in the integrand of the I_{xx}^* integral, which is proportional to $\mu_{\perp}(2p_z \leftarrow 2p_x)$.

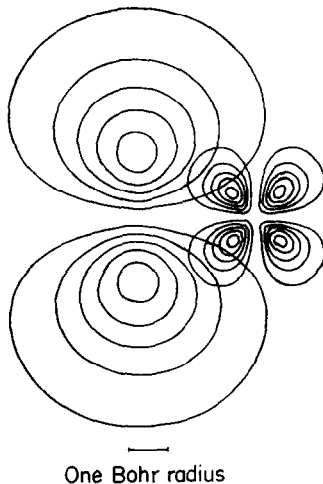


FIG. 2. Contour map of factors $\langle 2p_x(\text{Li}) |$ and $x | 2p_z(\text{F}) \rangle$ in the integrand of I_{xz}^* integral, which is proportional to $\mu_{\perp}(2p_x \leftarrow 2p_z)$ and to the integral term in $\mu_{\parallel}(2p_x \leftarrow 2p_z)$.

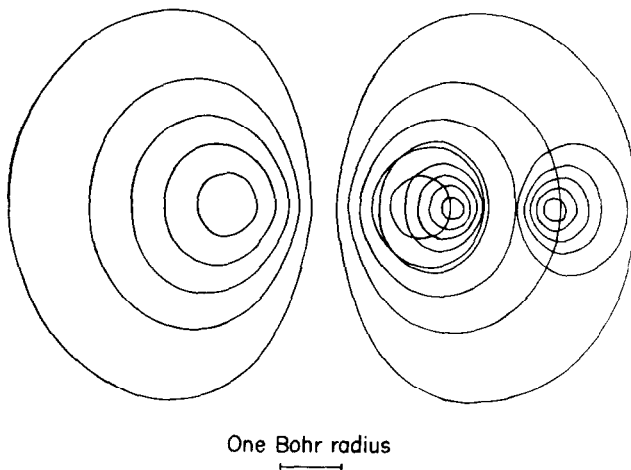


FIG. 3. Contour map of factors $\langle 2p_z(\text{Li}) |$ and $z | 2p_z(\text{F}) \rangle$ in the integrand of I_{zz}^* integral, which is proportional to the integral term in $\mu_{\parallel}(2p_z \leftarrow 2p_z)$.

Destructive interference is again severe in the integrand of I_{zz} , as the $2s$ orbital is swallowed up in one of the lobes of the $3d_{z^2}$ orbital of Eq. (8c). In the integrand of I_{xx} , however, the overlap of the $3p_x$ and $2p_x$ orbitals of Eq. (8e) is wholly constructive.

The numerical results obtained from Eqs. (6) and (8) for LiF are given in Table II. Values of the overlap integrals are also included. The calculations were re-

TABLE I
DIPOLE INTEGRALS FOR $\text{LiF} \rightarrow \text{Li}^* + \text{F}$ TRANSITIONS

Fig. No. ^a	$\int \text{LRd}\tau$	L (on left)	R (on right)
1	I_{zz}^*	$\langle 2p_z(C_{\text{Li}}) x$	$ 2p_x(C_{\text{F}}) \rangle$
2	I_{zz}^*	$\langle 2p_x(C_{\text{Li}}) $	$x 2p_z(C_{\text{F}}) \rangle$
3	I_{zz}^*	$\langle 2p_z(C_{\text{Li}}) $	$z 2p_z(C_{\text{F}}) \rangle$

^a In the figures contour maps are plotted for values of the coordinates such that $|L|^2/|L_{\text{max}}|^2$ or $|R|^2/|R_{\text{max}}|^2 = 0.1, 0.3, 0.5, 0.7,$ and 0.9 . The Li atom is on the left and separated from the F atom by the equilibrium internuclear distance.

TABLE II
TRANSITION DIPOLES AND OSCILLATOR STRENGTHS FOR PHOTODISSOCIATION OF LiF

Type of transition ^a		$\langle \text{Li} \text{F} \rangle$ overlap	$\mu_{if} = e f_{if}^+$ Debyes	f , Oscillator strength
Transitions which produce an excited Li atom				
\parallel, I_{zz}^*	$(2p_z)_{\text{F}} \rightarrow (2p_z)_{\text{Li}}$	-0.07	-0.01+	0.120
\parallel, I_{zz}^*	$(2p_x)_{\text{F}} \rightarrow (2p_x)_{\text{Li}}$	0.12	0.34+	0.240
\perp, I_{zz}^*	$(2p_z)_{\text{F}} \rightarrow (2p_x)_{\text{Li}}$	0.00	0.34	0.0069
\perp, I_{xx}^*	$(2p_x)_{\text{F}} \rightarrow (2p_z)_{\text{Li}}$	0.00	-2.05	0.254
Transitions which produce a normal Li atom				
\parallel, I_{zz}	$(2p_z)_{\text{F}} \rightarrow (2s)_{\text{Li}}$	-0.06	0.04+	0.094
\perp, I_{xx}	$(2p_x)_{\text{F}} \rightarrow (2s)_{\text{Li}}$	0.00	1.43	0.096

^a For each transition involving a p_x orbital there is a corresponding transition (not listed) of equal intensity involving a p_y orbital. The plus sign attached to the values for parallel transitions indicates that the term $\alpha e r_0$ must be added to obtain the total transition dipole moment. The oscillator strengths correspond to $\mu_{\parallel} = 2.0$ D and to frequencies of $50\,000\text{ cm}^{-1}$ and $64\,000\text{ cm}^{-1}$, respectively, for the transitions which produce a normal or an excited Li atom.

peated using the orbital exponents determined by new rules recently offered by Clementi and Raimondi (11), which increase the effective nuclear charge on Li from 1.2 to 1.2792 and decrease that on F from 5.2 to 5.0909. The results changed by only about 10% or less, however.

Table II nicely confirms the qualitative conclusions obtained from Figs. 1-3, as the dipole integrals which contribute to parallel transitions are much smaller than those which contribute to the perpendicular transitions. However, the values of μ_{if} given in Table II correspond to the limit $\alpha \ll 1, \beta \ll 1$, or "100% ionic bonding" in the ground electronic state and "100% atomic bonding" in the excited states. The additional term $\alpha e r_0$ given in Eq. (6) must be added to obtain the transition moment for the parallel transitions, as indicated by the plus signs in Table II. At the equilibrium internuclear distance, 1.564 Å, this term is 7.51α Debye units. Even a modest amount of mixing of the ionic and

atomic character is sufficient to make μ_{\parallel} comparable to μ_{\perp} ; thus $\alpha er_0 > 1$ Debye if $\alpha \gtrsim 0.13$, which corresponds to a deviation of only $\alpha^2/(1 + \alpha^2) \gtrsim 2\%$ from 100% ionic character in the ground electronic state.

It is quite likely that mixing of this extent does occur, although the model provides no satisfactory way to assign a definite value to the parameter α . The traditional primitive estimate of partial ionic character (12, 13) compares the observed permanent dipole moment μ_0 with the value er_0 expected for a pair of rigid ions. According to this (13), the ionic character of the ground electronic state is $\lambda^2/(1 + \lambda^2)$, where

$$\mu_0/er_0 = (\lambda^2 - 1)/(1 + \lambda^2 + 2\lambda\langle\phi_A | \phi_B\rangle), \quad (9)$$

and in terms of our wave functions, $\alpha \simeq 1/\lambda$. The overlap integral evaluated from Slater orbitals is negligible. Thus from the experimental dipole moment (14), $\mu_0 = 6.284$ D, we find $\alpha \simeq 0.27$ (i.e., 93% ionic character) and $\alpha er_0 = 2.02$ D for LiF. It should be noted, however, that for alkali halides the observed values of $\mu_0/er_0 < 1$ are probably due mainly to the effect of polarization of each ion in the electric field of the other (15) rather than to deviations from purely ionic bonding. A polarizable ion model provides an accurate correlation of many spectroscopic properties of the alkali halides (16, 17). In the present model, the effect of polarization would be included in the mixing parameter α and hence is more or less equivalent to reducing the ionic character.

Also included in Table II are the oscillator strengths (8) calculated from

$$f = 4.707 \times 10^{-7} g \nu_{ij}^2 |\mathbf{u}_{ij}|^2, \quad (10)$$

where the transition frequency ν_{ij} is in cm^{-1} and the transition dipole in Debye units. The orbital degeneracy factor $g = 2$ for the transitions which involve a p_x orbital on either or both the atoms (to allow for the corresponding p_y orbital) and $g = 1$ otherwise. For the parallel transitions the f -values are essentially proportional to α^2 (aside from the small contributions from the eI_{ij} terms listed in Table II) and the transition dipole has been arbitrarily set equal to 2.0 Debye, which corresponds to $\alpha \simeq 0.22$ –0.26.

DISCUSSION

The model treated here is a straightforward extension of Mulliken's discussion (8) of the charge transfer transitions in H_2^+ and H_2 . There is a curious relation between his results for these prototype homopolar cases and our intrinsically heteropolar model. As noted, Mulliken found for H_2^+ essentially Eq. (5). For H_2 he obtained the same result with an additional factor of $2^{1/2}$, which arose because either electron could make the jump. In our case we also find this factor of $2^{1/2}$ appearing before the transition dipole integrals in Eq. (6); these terms correspond to transitions from the ionic structure A^+B^- to the shared pair structure $A:B$ and either electron may shift. However, the $2^{1/2}$ factor is absent from the term αer_0 of Eq. (6) and from Eq. (5); these correspond to transitions between

the mixed structures, $(A+B^- \pm A:B)$, and in effect one electron is tied down in maintaining the correlation. Thus in a sense this model is intermediate between H_2^+ and H_2 .

In the homopolar cases and in the equal mixing limit of the present model, Eq. (5), only parallel charge transfer transitions are allowed. In contrast, for unequal mixing, Eq. (4), both parallel and perpendicular transitions will occur when p orbitals are involved. When there is no mixing, Eq. (6), most of the intensity is found in the perpendicular transitions, but even a small amount of mixing is enough to put comparable intensity into the parallel transitions. Within the severe idealizations of the model itself, these qualitative features appear to be insensitive to the various assumptions which were made to obtain numerical results. In particular, the inequalities among the transition integrals depend only on the general size and shape of the orbitals.

The charge transfer model is expected to give similar results for the analogous transitions of other alkali halides, although calculations have not been carried out. The overlaps which determine the transition dipoles depend mainly on the relative scale and separation of the M and X orbitals. Thus the pattern found in Table II is probably typical, since the effective nuclear charge parameters C_M and C_X remain about the same for all the alkali halides and the increase in bond length with size of M and X is offset by the expansion in scale which accompanies an increase in the principal quantum numbers. Similar transitions occur in the spectra of hydrogen halides, but the simple model may be inappropriate as the ground states of these molecules are far from 100% ionic.

Our heavy use of the word is intended to emphasize that a "model" may prove to have properties very different from a molecule. However, as a simple reference case, the model suggests that the possibility of observing anisotropy in the photodissociation of alkali halides depends primarily on the extent of mixing of ionic and atomic character in the ground and excited states. A small amount of mixing ($\sim 5\%$) would account for the lack of anisotropy indicated by the experiments available at present and is compatible with chemical and spectroscopic evidence. Recently, accurate values of the dissociation energy and dipole moment of the ground electronic state of LiF have been predicted from a self-consistent-field wave function (18), and it will be interesting to test the results of the simple model when a wave function of comparable quality is obtained for an excited state.

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REFERENCES

1. R. N. ZARE AND D. R. HERSCHBACH, *Rev. Mod. Phys.* (to be published).
2. R. N. ZARE AND D. R. HERSCHBACH, *Proc. I.E.E.E.* **51**, 173 (1963); also University of California Radiation Laboratory Report UCRL-10438 (February, 1963).

3. R. S. MULLIKEN, *Phys. Rev.* **50**, 1017, 1028 (1936); **51**, 310 (1937).
4. A. C. G. MITCHELL, *Z. Physik* **49**, 228 (1928).
5. H. G. HANSON, *J. Chem. Phys.* **27**, 491 (1957).
6. For a review, see R. W. Nicholls and A. L. Stewart, in "Atomic and Molecular Processes," pp. 61-64. D. R. Bates (ed.). Academic Press, New York, 1962.
7. S. EHRENSON AND P. E. PHILLIPSON, *J. Chem. Phys.* **34**, 1224 (1961).
8. R. S. MULLIKEN, *J. Chem. Phys.* **7**, 20 (1939). See also G. Herzberg, "Spectra of Diatomic Molecules," pp. 199-201, 381-386. Van Nostrand, Princeton, New Jersey, 1950.
9. H. EYRING, J. WALTER, AND G. E. KIMBALL, "Quantum Chemistry," pp. 162-163. Wiley, New York, 1944.
10. SHARE distribution program D1 BC DIAT, available from SHARE Librarian, IBM, White Plains, New York.
11. E. CLEMENTI AND D. L. RAIMONDI, *J. Chem. Phys.* **38**, 2686 (1963).
12. L. PAULING, "Nature of the Chemical Bond," 3rd ed., pp. 78 and 99. Cornell Univ. Press, Ithaca, New York, 1960.
13. C. A. COULSON, "Valence," 2nd ed., pp. 107-110. Oxford Univ. Press, London and New York, 1961.
14. L. WHARTON, W. KLEMPERER, L. P. GOLD, R. STRAUCH, J. J. GALLAGHER, AND V. E. DERR, *J. Chem. Phys.* **38**, 1203 (1963).
15. E. S. RITTNER, *J. Chem. Phys.* **19**, 1030 (1951).
16. A. HONIG, M. MANDEL, M. L. STITCH, AND C. H. TOWNES, *Phys. Rev.* **96**, 629 (1954).
17. W. A. KLEMPERER AND S. A. RICE, *J. Chem. Phys.* **26**, 618 (1957); **27**, 573 (1957).
18. A. D. MCLEAN, *J. Chem. Phys.* **39**, 2653 (1963).