

the triple-dipole contribution to the energy of the linear lattice is about 1% of the second-order contribution. Axilrod⁵ found that, in xenon's close-packed lattice, the triple-dipole contribution is about 9% of the experimental cohesive energy (which, in turn, happens to be about equal to the calculated second-order energy). This increase by a factor of 9 upon passing from a one-dimensional to a three-dimensional lattice is due to the increase, relative to the number of pairs, of the number of triplets of atoms. In the linear lattice, only one triplet can be formed from a central atom and its two nearest neighbors; in a close-packed space lattice, the corresponding number is 66. The number of pairs correspondingly increases from 2 to 12. The ratio of the two factors (66/1) and (12/2) is 11, which value agrees with the actual factor 9 much better than one might

expect in view of the crudity of the argument. This discussion suggests that, in the transition from the linear lattice to three-dimensional lattices, the fourth- and higher-order contributions to the lattice energy may increase in relative importance even more strikingly than the third-order contribution does.

The foregoing investigation of the cohesive energy of a linear lattice does not give any quantitative information about actual molecular crystals, principally because a one-dimensional arrangement fails to give free play to the combinatorial possibilities of the many-body forces, but also because of the shortcomings of the model used. However, the results do suggest that, in materials for which α/a^3 is fairly large, the contributions to the lattice energy due to higher order perturbations than the second may be of considerable importance.

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Interaction of Vibrational and Electronic Motion in Alkali Halide Molecules

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A treatment is developed to interpret the observation that in corresponding regions of the ultraviolet the absorption spectra of sodium iodide and potassium iodide show a band system and a continuum, respectively. The former results from a bound excited state in which the form of the electronic wave function changes drastically with internuclear distance. The latter arises because the nuclear motion can no longer be considered adiabatic with respect to electronic motion, so that the noncrossing rule does not apply.

I. INTRODUCTION

IN their lowest electronic states, the diatomic alkali halide molecules seem to behave essentially like pairs of oppositely charged ions. Calculations based on an ionic model¹⁻³ do agree well with some experimentally determined quantities, such as dissociation energies, vibration-rotation coupling constants and variation of dipole moment with vibrational state or internuclear distance. With the help of such a model, one may construct potential energy curves which describe molecular properties for internuclear separations close to the equilibrium separation.

A Coulombic potential energy curve cannot, however, give a correct picture of the interatomic forces if the nuclei are widely separated or if the vibrational quantum number is very high. When any alkali halide molecule is adiabatically dissociated, the products must be two uncharged atoms in their ground states, rather than two oppositely-charged ions. This comes about because it is always possible to construct from $M^0(^2S) + X^0(^2P_{1/2})$ a

state of $^1\Sigma^+$ symmetry, and since the ionic dissociation limit always lies higher in energy than the atomic, the noncrossing rule will apply. In the same manner, it is clear that any excited molecular state of $^1\Sigma^+$ symmetry whose dissociation limit is energetically lower than the level corresponding to two ions must be at least partially ionic for some region of internuclear separation.

From these considerations, one may draw potential curves like those of Figs. 1 and 2, which show the behavior of some of the states of NaI and KI which have the same symmetry as the molecular ground states. The ground states are appropriately denoted as $^1\Sigma^+$, in the notation of Hund's case (*a*) coupling. Here both Λ , the component of orbital angular momentum along the internuclear axis, and Σ , the corresponding component of total spin angular momentum, are both good quantum numbers. Possibly, the excited states should also be described in this way, but it may be that only Ω , the resultant of Λ and Σ , is a good quantum number. In this case, Hund's case (*c*) notation should be used, and the excited states would be denoted as O^+ .

The point at which the ionic curve would cross the lowest nonionic curve, denoted henceforth as the "crossing point" or R_x , lies generally at a fairly large internuclear distance (Table I). As a result, and this

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¹ E. S. Rittner, *J. Chem. Phys.* **19**, 1030 (1951).

² Honig, Mandel, Stitch, and Townes, *Phys. Rev.* **96**, 629 (1954).

³ S. A. Rice and W. Klemperer, *J. Chem. Phys.* **26**, 573 (1957).

will be shown in the next sections, the molecular states change character rather abruptly, from ionic to nonionic, as the internuclear separation passes through the small neighborhood of ca 0.5 to 0.001 Å about the crossing point. The ground state is not observably affected by this phenomenon under any conditions yet encountered; its potential well is so deep that even vibrational levels of $v''=20$ or more seem to lie entirely within the ionic region of the curve. Suppose, however, that a molecule be excited optically to its first O^+ state. For example, we may consider the first excited state shown in Fig. 1. From the crossing point R_x to the next point of intersection R_x' , this state is essentially ionic; for distances shorter than R_x , the state is predominantly nonionic. The transition region is qualitatively as shown by the dotted curves. In the excited state, the attractive forces

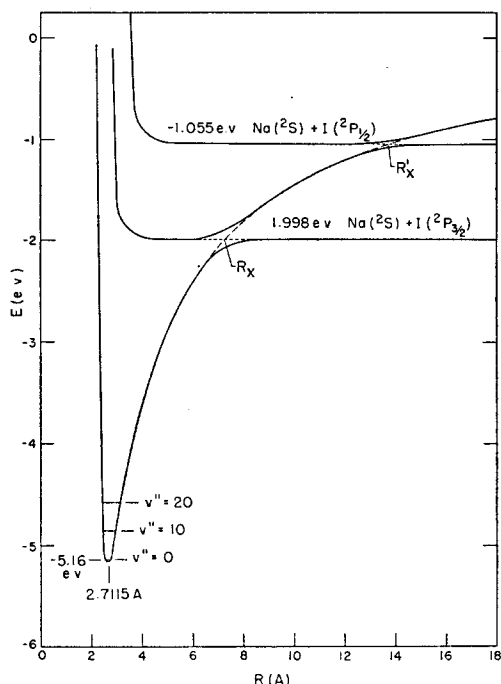


FIG. 1. Potential curves for sodium iodide.

arise primarily from Coulombic interaction occurring to the right of R_x . Considering the motion of the nuclei to be classical for the moment, one might picture the behavior of the molecule as follows: absorption of light carries the system vertically from the ground state to the O^+ excited state, and produces a change in the electronic wave function corresponding to the transfer of an electronic charge along the internuclear axis from the halide to the metal. The nuclei move apart across the relatively flat region of potential energy toward R_x . Just as the crossing point region is reached, the electronic wave function readjusts itself, and, effectively, an electron jumps back from the metal to the halogen. Electrostatic forces are rapidly set up which pull the nuclei back toward each other. As the nuclei pass the

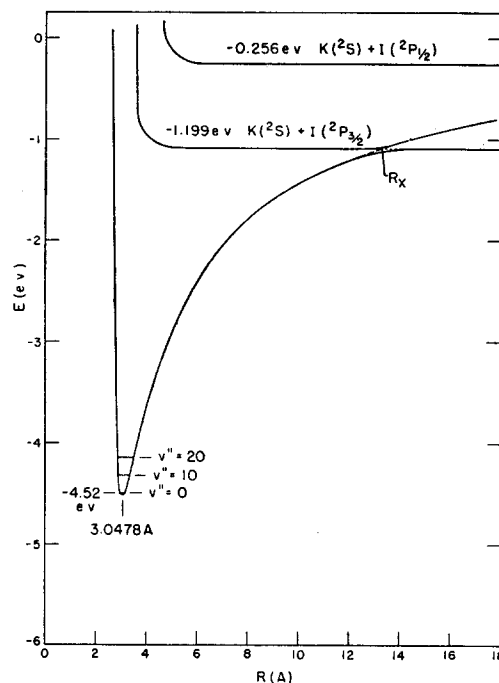


FIG. 2. Potential curves for potassium iodide.

crossing point again, the electron returns to the metal, and the two particles, now neutral, come together once more.

The process just described is based on the adiabatic hypothesis, namely that the electrons move fast enough compared with nuclei to behave by themselves as a closed system with the internuclear distance as a parameter. This implies that the electronic motion is separable from that of the nuclei and that the electronic charge cloud is described at any internuclear distance by an eigenfunction of the electronic Hamiltonian. If the alkali halide molecules in their first excited O^+ states do satisfy this hypothesis, then our description must be approximately correct for the motion of the electrons during a single vibration. One may, however, question the validity of the hypothesis on the following ground. Electronic velocities are roughly 1800^1 or about 40 times nuclear velocities. Therefore in the time that the nuclei move 0.1 Å, the electrons can move about 4 Å. Hence if the crossing point region occurs at a separation of 20 Å, say, and is 0.1 Å wide, an electron cannot be expected to make a successful jump. This means that the electronic charge will not be described by the

TABLE I. R_x : Internuclear separations at crossing points (distances in Bohr radii a_0).

	F	Cl	Br	I
Li	15.372	16.393	14.322	12.094
Na	17.902	19.299	16.531	13.619
K	37.846	44.535	32.126	22.695
Rb	48.940	60.739	39.783	26.266
Cs	108.843	191.63	71.986	37.275

eigenfunctions of the electronic Hamiltonian alone, and its motion will not be separable from that of the nuclei.

According to the following considerations, one may determine immediately from its electronic absorption spectrum whether a given alkali halide molecule does satisfy the adiabatic hypothesis. If the electrons do follow perfectly as the nuclei move, then the first excited O^+ state will have bound levels; in Fig. 1, these would lie between -2 and -1 ev. The transition from the ground state to this state is strongly allowed, so that the electronic spectrum should show a series of bands. If, on the other hand, the electrons cannot follow the nuclear motion, then the two nuclei will find themselves to the right of R_x as two neutral particles. This corresponds to two atoms in their ground states, or to a continuum level belonging to the ground electronic state determined according to the adiabatic hypothesis. In this case, the ultraviolet absorption spectrum would contain a continuum lying to the red of the adiabatically determined dissociation limit. This latter possibility is an apparent violation of the noncrossing rule, but, as will be shown below, can arise if the electronic motion fails to follow the nuclei.

In the observed spectra of the alkali halides, most of the absorptions appear as continua.⁴⁻⁷ According to the most recent identification of these spectra,⁸ most of the continua arise from normal photodissociation, wherein the absorbed radiation carries the molecular energy above the dissociation limit of the corresponding state. For KI, however, the first strong continuum lies well to the red of dissociation limit of a state dissociating to $K(^2S) + I(^2P_{3/2})$. And for NaI, instead of a continuum, a very rich band spectrum appears; this was observed by Sommermeyer⁴ and Levi,⁶ and re-examined under high dispersion by the present author.⁹ This note is an attempt to rationalize these observations, and in particular, to show that the first parallel charge-transfer absorption of KI is due to a violation of the noncrossing rule, and that the corresponding absorption process in NaI produces an excited state in which the electron distribution is a sensitive function of internuclear distance.

II. FORMAL SOLUTION OF THE COUPLING PROBLEM

We shall follow a treatment here which is quite similar to one of London¹⁰ which deals with the collision of an alkali atom with a halogen atom. From the outset, it is assumed that it is necessary to consider only two electronic states of the molecule, which in zero order may be taken as the state composed of two ions M^+ and X^- , and the lower O^+ state derived from two atoms in their ground states, $M^0(^2S)$ and $X^0(^2P_{3/2})$. Here, M

represents the alkali metal (Li, Na, K, Rb, or Cs) and X , the halogen (F, Cl, Br, or I). We represent the ionic state as ψ_1 and the nonionic state as ψ_2 . Later we shall treat ψ_1 as a product of single-ion wave functions $\phi(M^+)$ and $\phi(X^-)$, and ψ_2 as a product of atomic functions $\phi(M^0)$ and $\phi(X^0)$. It is assumed also that any non-orthogonality of ψ_1 and ψ_2 is negligibly small.

The functions ψ_1 and ψ_2 are not eigenfunctions of the electronic Hamiltonian for fixed nuclei; their diagonal matrix elements become equal at R_x and they both have the same symmetry. New functions Ψ_A and Ψ_B may be obtained from ψ_1 and ψ_2 as follows. Let

$$\Psi_A = \psi_1 \cos \omega + \psi_2 \sin \omega, \quad (1a)$$

$$\Psi_B = -\psi_1 \sin \omega + \psi_2 \cos \omega. \quad (1b)$$

Then the Schroedinger equation for the electronic wave functions may be written as

$$\mathcal{H}_0 \Psi = \left[\sum_{\text{electrons}} \frac{p_i^2}{2m} + V(r, R) \right] \Psi = \epsilon(R) \Psi. \quad (2)$$

Here p_i is the momentum operator for the i th electron, m is the electronic mass, V is the potential energy operator including electron-electron, electron-nuclear, and nuclear-nuclear interaction, ϵ is the appropriate energy eigenvalue, r denotes the set of electronic coordinates and R is the internuclear distance. Equation (2) may be solved to give ϵ and ω as functions of R and the functions Ψ_A and Ψ_B which will be accurate to first order. If Ψ_A is chosen to be the molecular ground state, then ω will take on values from zero (near the equilibrium internuclear distance) to $\pi/2$ (at very large separations).

The vibrational wave functions χ may now be introduced. We write the electronic-plus-vibrational or vibronic wave functions as products:

$$\Theta_{Am}(r, R) = \Psi_A(r, R) \chi_{Am}(R) \quad (3a)$$

and

$$\Theta_{Bn}(r, R) = \Psi_B(r, R) \chi_{Bn}(R). \quad (3b)$$

The functions χ_{Am} and χ_{Bn} are the m th and n th vibrational wave functions appropriate to electronic levels A and B , respectively, if A and B are assumed to be true stationary states. We may let the free particle wave functions χ_A be approximated by a discrete set of wave packets¹¹ χ_{Am} .

If the Born-Oppenheimer approximation¹² held for the alkali halides, one could write the equation for the vibronic energy,

$$\begin{aligned} \mathcal{H} \Theta_{Am} &= (\mathcal{H}' + \mathcal{H}_0) \Theta_{Am} \\ &= \Psi_A \left[\frac{-\hbar^2}{2M} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right] \chi_{Am} + \mathcal{H}_0 \Psi_A \chi_{Am} \quad (4) \\ &= E_{Am} \Psi_A \chi_{Am}, \end{aligned}$$

⁴ K. Sommermeyer, *Z. Physik* **56**, 548 (1929).

⁵ H. D. Schmidt-Ott, *Z. Physik* **69**, 724 (1931).

⁶ H. Levi, Doctoral dissertation, Berlin, 1934.

⁷ R. S. Berry and W. Klemperer, *J. Chem. Phys.* **26**, 724 (1957).

⁸ Klemperer, Berry, and Rice (to be published).

⁹ R. S. Berry (to be published).

¹⁰ F. London, *Z. Physik* **74**, 143 (1932).

¹¹ E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 165 ff.

¹² M. Born and R. Oppenheimer, *Ann. Phys.* **84**, 457 (1927).

and similarly for Θ_{Bn} . The operator \mathcal{H}' in brackets corresponds to the nuclear kinetic energy; M is the reduced mass of the nuclei.

In fact, the operator \mathcal{H}' does connect Ψ_A and Ψ_B , so that the Hamiltonian is not strictly diagonal in a Θ_{Am} , Θ_{Bn} representation. Moreover, the vibronic energy of any excited state Bn is overlapped by the continuum of energies of the state A . Were it not for this degeneracy, the energy of each upper state Bn could be evaluated by second-order perturbation theory. As it is, a full solution of the problem would require construction and solution of the secular equation for the set of functions Θ_{Am} and Θ_{Bn} . As the next section will show, however, it is not necessary to solve the secular equation to get a qualitative picture of the coupling phenomenon; an examination of the off-diagonal elements of the Hamiltonian matrix will suffice. Alternatively, the formalism of time-dependent perturbation theory might be used. This is the method used by London,¹⁰ but again for the purposes of the present treatment, an exact solution is intractable and unnecessary.

The packet-functions Θ_{Am} and the bound-state functions Θ_{Bn} are chosen to form an orthonormal set of solutions to Eq. (4). The considerations below are limited to the interaction of a single bound function with a finite energy band of dissociative functions. Only a finite set of packets is necessary to cover this energy band. (The accuracy with which the interaction terms may be determined depends upon the band width allotted to each packet.¹¹) Under these conditions the secular equation takes this form

$$\det \begin{vmatrix} E_{A1} - E & 0 & 0 & H_{A1Bn} \\ 0 & E_{A2} - E & 0 & H_{A2Bn} \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & H_{ArBn} \\ \vdots & \vdots & \vdots & \vdots \\ \dots & \dots & E_{Ar} - E & H_{ArBn} \\ \vdots & \vdots & \vdots & \vdots \\ H_{BnA1} & H_{BnA2} & H_{BnAr} & E_{Bn} - E \end{vmatrix} = 0. \quad (5)$$

The elements $H_{Bn \cdot Am}$ and $H_{Am \cdot Bn}$ are the perturbation terms arising when the nuclear momentum operator acts on the electronic wave functions. Explicitly, one may write

$$H'_{Am \cdot Bn} = -\frac{\hbar^2}{2M} \int \Psi_{AXAm} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \Psi_{BXBn} d\tau. \quad (6)$$

We may drop the subscripts m and n for the present. In order that the Hamiltonian remain real, we rewrite \mathcal{H} as $\frac{1}{2}(\mathcal{H} + \mathcal{H}^+)$, so that the perturbation matrix elements become $(H_{AB} + H_{BA}^*)$. (The operator \mathcal{H}^+ is the Hermitean conjugate of \mathcal{H} , and H_{BA}^* is the complex conjugate of H_{BA} .) The wave functions χ_B may be chosen real, and the packet functions χ_A , imaginary. If the variation (e.g., polarization) of the zero-order func-

tions ψ_1 and ψ_2 with internuclear distance is neglected, the matrix elements may be reduced to the form

$$\begin{aligned} & \frac{1}{2}(H_{AB} + H_{AB}^+) \\ &= -\frac{\hbar^2}{2M} \iiint \frac{d\omega}{dR} \left(\dot{\chi}_B^* \frac{d\chi_A}{dR} - \chi_A^* \frac{d\chi_B}{dR} \right) \\ & \times R^2 \sin\theta dR d\theta d\varphi = -\frac{\hbar^2}{2M} \int \frac{d\omega}{dR} f(R) dV. \quad (7) \end{aligned}$$

The absolute square of this matrix element is the measure of the degree to which the states Θ_A and Θ_B mix. That is to say, $\frac{1}{2}(H_{AB} + H_{AB}^+)^2$ fixes the probability that a molecule excited to state B from state A will dissociate into a continuum level of state A , instead of remaining in B .

In most molecules, the integral of Eq. (6) is so small that it may be entirely neglected. This is the general case because $d\omega/dR$ generally varies quite slowly compared with the rate of oscillation of the second factor. In an alkali halide, however, $d\omega/dR$ is quite peaked in the region of the crossing point; consequently the wave nature of the nuclear momentum term is unimportant, the integral is sizeable and the molecule may dissociate.

III. THE PERTURBATION MATRIX ELEMENTS

An exact evaluation of the matrix element of (7) is hardly feasible. The proper vibrational wave functions for the upper state are unknown, and likewise, a truly exact expression for $d\omega/dR$ is not at hand. One may proceed, nonetheless, to examine the behavior of the integrand of (7) in the region of the crossing point. Even from such crude approximations as are available, it is possible to distinguish the behavior of potassium iodide and most of the other alkali halides from that of sodium and lithium iodides. We may proceed by evaluating $d\omega/dR$, and then by examining the second factor which depends on the vibrational wave functions. In handling the term $\chi_B^*(d/dR)\chi_A - \chi_A^*(d/dR)\chi_B$, we shall treat the functions χ_A of the lower state as continuum functions because explicit use of packet functions merely introduces damping factors and extra terms having the same qualitative behavior as the sinusoidal continuum functions.

The function $d\omega/dR$ is evaluated as follows: the electronic 2×2 secular equation based upon the Hamiltonian of Eq. (3) leads to an expression giving ω in terms of the Hamiltonian matrix elements. The diagonal matrix elements and derivatives are easily determined for internuclear distances comparable with that of the crossing point because the ionic function gives a Coulombic energy, and the nonionic function is simply a constant. The off-diagonal elements and their derivatives are approximated in terms of the overlap integral (and its derivatives) between a $5p\sigma$ orbital on the halogen ion and an ns orbital on the alkali atom. This is

a procedure used by Magee¹³ in a treatment of reactions of the alkali halides.

In detail, if Ψ_A and Ψ_B are written as in Eqs. (1a) and (1b), the secular equation takes the form

$$\det \begin{vmatrix} H_{11}^0 - E & H_{12} \\ H_{12} & H_{22}^0 - E \end{vmatrix} = 0. \quad (8)$$

The solutions lead to

$$\tan(2\omega) = 2H_{12}/(H_{11} - H_{22}). \quad (9)$$

If the zero of energy is chosen as the level of $M^+ + X^-$, then $-Q$, the difference between the electron affinity of the halogen and the ionization potential of the alkali metal, is the energy of the ground state atoms. Since the internuclear distances at the crossing points as shown in Table I are so large, one is justified in letting

$$H_{11} = -Q. \quad (10)$$

Similarly, we let

$$H_{22} = -e^2/R. \quad (11)$$

The approximation of reference 13 may be written as

$$\begin{aligned} H_{12} &= \int \phi(M^0)\phi(X^0)\mathcal{H}^0\phi(M^+)\phi(X^-)d\tau \\ &\cong \int m(1)x(2) \left[\frac{1}{r_{12}} - \frac{1}{r_{1x}} - \frac{1}{r_{2m}} + \frac{1}{R} \right] x(1)x(2)d\tau_1d\tau_2 \\ &= \frac{S_{m_x}}{R} - S_{m_x} \int x(2) \frac{1}{R_{2m}} x(2)d\tau_2 \\ &\quad + \int m(1)x(2) \frac{1}{r_{12}} x(1)x(2)d\tau_1d\tau_2 \\ &\quad - \int m(1) \frac{1}{r_{1x}} x(1)d\tau_1. \quad (12) \end{aligned}$$

Here, $m(1)$ denotes electron 1 in an outer s -orbital on the alkali nucleus, $x(2)$ denotes electron 2 in an outer $p\sigma$ orbital in a halogen, and S_{m_x} is the overlap between the two orbitals. We assume, after Magee, that the integral may be further approximated for short ranges at long distances as

$$H_{12} = S_{m_x}/cR, \quad (13)$$

where we have considered values for the constant c of 2, 5, and 8. The behavior of $d\omega/dR$ is relatively insensitive to the value of c , in any case. Upon substitution of (10), (11), and (13) into (9) and taking the derivative with respect to internuclear distance, one arrives at the expression

$$\frac{d\omega}{dR} = \frac{C}{c^2R^2[(e^2/R) - Q]^2 + 4S^2} \left[RS' \left| \frac{e}{R} - Q \right| + SQ \right]. \quad (14)$$

¹³ J. L. Magee, J. Chem. Phys. 8, 687 (1940).

The subscripts have been dropped from S_{m_x} , S' denotes the derivative with respect to R , and the absolute value of $[(e^2/R) - Q]$ is used to retain the principle value of $d\omega/dR$.

For sodium iodide, the overlap integral and its derivative have been evaluated exactly with one-electron Slater functions.¹⁴ For potassium iodide, however, the integration is only an approximation, because the non-integral effective quantum number of potassium prevents a solution in closed form. An approximation useful for large internuclear separations is given in the appendix.

The behavior of $d\omega/dR$ for NaI and KI in the region of their crossing points is given in Fig. 3. Values plotted correspond to a value of 5 for the constant c ; the behavior is almost identical with constants of 2 or 8, with peaking more pronounced for the high value of c . It should be particularly noted that $d\omega/dR$ is considerably broader for NaI than for KI. The area under $d\omega/dR$ is the same for both, but the peak height for KI is greater by a factor of ten than that for NaI, and the width, correspondingly smaller. This extra width, corresponding to a more gradual transition from nonionic to ionic behavior, is due primarily to the fact that at the crossing point, the iodide $5p\sigma$ orbital overlaps the sodium $3s$ orbital much more than it does the potassium $4s$ orbital (see Table II).

The vibrational part f of the integrand can only be estimated very crudely. The main point of interest is the wavelength with which the function oscillates. If this wavelength is comparable to or shorter than the half-width of $d\omega/dR$, then the integral (8) will be small and so will the probability of dissociation. If, on the other hand, the wavelength of f is long compared with the half-

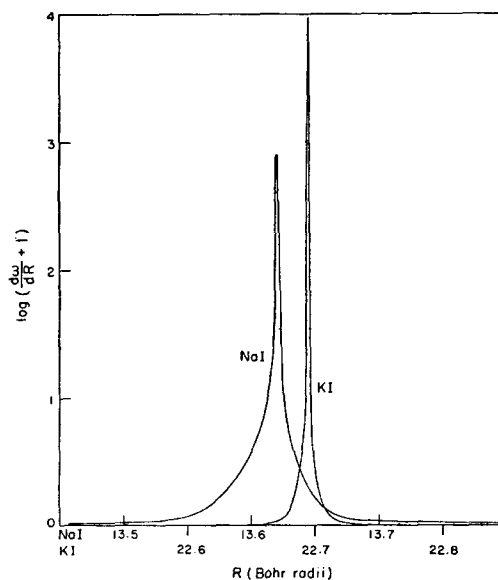


FIG. 3. The behavior of $d\omega/dR$ for sodium and potassium iodides.

¹⁴ Mulliken, Rieke, Orloff, and Orloff, J. Chem. Phys. 17, 1248 (1949).

TABLE II. Overlap and overlap derivatives at the crossing points.

	S	$R_e(dS/dR)$
NaI	3.2×10^{-3}	0.10
KI	1.6×10^{-4}	-1.1×10^{-2}

width of $d\omega/dR$, then the excited molecule will pass nonadiabatically through the region in which an adiabatic system would turn from nonionic to ionic.

To estimate the wavelength of the oscillatory nuclear function, we approximate the vibrational function of the upper state as a harmonic oscillator function, and consider its interaction with a monoenergetic, unnormalized sine wave. Let

$$\chi_B = B_n e^{-\alpha/2} (R - R_e)^2 H_n[\alpha^{1/2}(R - R_e)],$$

$$\alpha = 2\pi M \nu_e / \hbar,$$

and

$$\chi_A = i \sin k(R - u);$$

then

$$f = \chi_B \frac{d\chi_A}{dR} - \chi_A \frac{d\chi_B}{dR}$$

$$= i B_n e^{-\alpha(R - R_e)^2 / 2} \left\{ \left[\frac{k \cos k(r - u)}{R - R_e} - \sin k(R - u) \left(\alpha + \frac{1}{(R - R_e)^2} \right) \right] H_n[\alpha^{1/2}(R - R_e)] \right.$$

$$\left. + \sin k(R - u) \frac{2n\alpha^{1/2}}{R - R_e} H_{n-1}[\alpha^{1/2}(R - R_e)] \right\}. \quad (15)$$

If ν_e for the upper state is taken as 36 cm^{-1} ,⁹ the vibrational quantum number $n \geq 5$, and R_e and u as 10 and 2 Bohr radii, respectively, then the nuclear factor (for energies corresponding to the observed spectra) has a wavelength of about 0.3 Bohr unit or less for both NaI and KI.

III. DISCUSSION

From the tables of $d\omega/dR$, it is seen that for KI, this function is larger than one over a region slightly less than 0.04 Bohr unit wide. For NaI on the other hand, $d\omega/dR$ has a half-width of about 0.13 Bohr unit. When these two widths are compared with the wavelength of about 0.3 Bohr unit of f , it is apparent that the corresponding matrix elements will be of altogether different orders of magnitude. The transition probability for dissociation of the excited state will clearly be much less for NaI than that for KI.

A vanishingly small perturbation term, however is not necessary for the appearance of a band spectrum. So long as the lifetime of the excited state is of the order of 10^{-10} sec or more (which may be compared with 10^{-8} sec for normal radiative lifetimes) the individual spectral

lines will appear to be narrow. In other words, only if the lifetime of the excited state is very short, 10^{-11} sec or less, will the spectral lines be broadened enough to give the appearance of a continuum. From the observations of reference 9, the vibrational frequency of the upper state seems to be about 35 cm^{-1} . Consequently, the fact that the NaI spectrum contains rotational lines at most 1 cm^{-1} wide implies that the upper state may execute, on the average, at least thirty vibrations. Potassium iodide, on the other hand, can be assumed to undergo direct photodissociation to atoms.

According to the foregoing treatment, it is conceivable that the sodium iodide spectrum could contain a continuum at very low energies. The continuum could appear when the nuclear momentum in the excited O^+ state is very low so that the wavelength of χ_B in (7) is large. Such a low momentum state could probably be excited only from very high vibrational levels of the ground electronic state, which in turn can only be populated by heating the sample vapor to very high temperatures. No such continuum has been reported although samples have been heated up to 1300°C ;⁹ actually, from about 3020 Å to as long wavelengths as 4200 Å, rotational structure is quite apparent.⁹ It might be noted that at about 4000 Å the well-known fluctuation bands set in.^{4,6,7} These are relatively weak and are not observed in high dispersion.

In the case of potassium iodide, rotational structure might appear in absorption due to transitions to O^+ states just below the -0.256 eV limit (see Fig. 2). In this region, the wavelength of χ_B is quite short, so that perhaps the integral of (7) is diminished in magnitude from its value for lower vibrational levels. On the other hand, the adiabatically determined potential well of the first excited O^+ state can only support a finite number of vibrational levels, so that possibly no χ_B function may exist with a wavelength short enough to allow a bound upper state to exist. No rotational structure has been reported for this spectrum, although Levi,⁶ using a low dispersion spectrograph, has reported a *kanelliertes* band system between 4090 and 5000 in chemiluminescence. These bands, however, seem to coincide with high members of the fluctuation band series, and no further mention is made of additional sharp structure.

The first strong continuum of KI has a maximum at about 3.83 eV and spreads rapidly to the red as the temperature of the sample is raised. As an alternative to the foregoing discussion, the position of the maximum might be explained in terms of slightly nonvertical transitions.¹⁵ The strong absorption further to the red has been re-examined by the author under high dispersion and shows no trace of structure. Consequently it is felt that nonvertical transitions do not provide a satisfactory explanation for the entire continuum.

One is tempted to predict the appearance of band spectra for two other alkali halides. An examination of Q

¹⁵ Coolidge, James, and Present, *J. Chem. Phys.* 4, 193 (1936).

TABLE III. Q : Differences between alkali ionization potentials and halogen electron affinities* (energies in ev).

	F	Cl	Br	I
Li	1.77	1.66	1.90	2.25
Na	1.52	1.41	1.646	1.998
K	0.719	0.611	0.847	1.199
Rb	0.556	0.448	0.684	1.036
Cs	0.25	0.142	0.378	0.73

* Ionization potentials are taken for Li, Na, K, and Rb from *Atomic Energy Levels*, Circular 467 (Department of Commerce, National Bureau of Standards, Washington, D. C., Vol. I, 1949; Vol. II, 1952). That for Cs was taken from G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944), p. 201. Electron affinities were taken from the following references: F: H. O. Pritchard, *Chem. Revs.* **52**, 529 (1953). Cl: K. J. McCallum and J. E. Mayer, *J. Chem. Phys.* **11**, 55 (1943). Br: P. M. Doty and J. E. Mayer, *J. Chem. Phys.* **12**, 323 (1944). I: P. P. Sutton and J. E. Mayer, *J. Chem. Phys.* **3**, 20 (1935).

(Table III), and the crossing distance for LiI make it apparent that this molecule should have a bound state spectrum, and LiBr perhaps also may show such an absorption. In the case of lithium iodide, experiments so far have only shown continua above the dissociation limit of the upper state. It seems that the repulsive part of the potential energy of the upper state in this salt is relatively further removed from the minimum of the ground state than is the corresponding curve in sodium iodide. The band spectrum of the lithium salt would only appear if the vapor sample were heated enough to populate rather high vibrational states. In the case of lithium bromide, the same holds true; here, however, the crossing point lies at a slightly larger internuclear distance than in NaI, and Q is likewise smaller. This molecule could, from the data available, behave either like potassium iodide or like sodium iodide with respect to its first strong absorption.

The excited electronic state discussed above is quite similar to the first excited $^1\Sigma$ state of LiH¹⁶ and the other alkali hydrides. Just as in the halide molecules, the ground state contains large ionic contributions but would dissociate adiabatically to uncharged atoms in their ground states. Similarly, the first $^1\Sigma$ excited state derives its binding from ionic contributions analogous to those of the first O^+ excited state of NaI, for example; the attractive part of the potential is like that between R_x and R_x' of Fig. 1. Mulliken¹⁷ has examined the problem of the lithium hydride spectrum. He has shown that the rather unusual potential constants found by Crawford and Jorgensen¹⁶ for the upper state are in all probability due to Coulombic attractions which set in only at large internuclear separations, just as with NaI. The analogy is not exact because the dissociation limits of the hydrides are not the same as those of the halides; the two systems are qualitatively extremely similar, nonetheless.

In the case of LiH, the dissociation limit $Li(^2P) + H(^2S)$ lies between those corresponding to ions and to ground state atoms, just as the $Na(^2S) + I(^2P_{1/2})$ limit of

Fig. 1 lies between the ionic and atomic ground state limits. In both the halide and hydride cases, the noncrossing rule may be applied at the point corresponding to R_x' in Fig. 1, and then the nuclear motion may be considered as a possible perturbation, as in the above analysis. The treatment of Rosenbaum¹⁸ indicates that in the hydride case the noncrossing rule is obeyed and the first $^1\Sigma$ excited state of LiH dissociates to $Li(^2P) + H(^2S)$. The present treatment suggests that KI violates the noncrossing rule at R_x' (beyond the diagram of Fig. 2), that NaI probably violates it also, and that LiI may still obey the rule at its R_x' . The strong continuum of LiI at 4 ev suggests that the noncrossing rule does apply at R_x' for this molecule.

It is perhaps instructive to compare the phenomenon described above with that of predissociation, particularly as it can arise from the "crossing" of two potential curves of the same symmetry. One example of this is the predissociation in the second positive system ($C^3\Pi_u \leftarrow B^3\Pi_g$) of N_2 due to the "crossing" of the C state by another $^3\Pi_u$ state.¹⁹ The C -state and the other $^3\Pi_u$ state which "crosses" it, rather than the B and C states, are to be compared with the ground and first excited O^+ states of the alkali halides. The C -state curve, like that of the ground state of NaI, would lead to a high-energy dissociation limit but for the repulsive state which intersects it. No nitrogen spectrum analogous to the blue bands of NaI have been observed however; such a transition for N_2 would be a $u \rightarrow u$ process and therefore forbidden. The predissociation of ICl described by Brown and Gibson²⁰ is another case in which two potential curves of the same symmetry seem, to a low degree of approximation, to cross. In this case, the angular momentum coupling is closer to Hund's case (c), so that the two states are appropriately labeled O^+ . The state directly observed in absorption spectra, actually $^3\Pi_{O^+}$, is again analogous to the ionic ground state of the alkali halides, and the repulsive O^+ state which causes the predissociation, to the first excited O^+ states of the alkali halides. Since ICl is heteronuclear, it is possible that a direct transition from the $^3\Pi_{O^+}$ state to the state causing predissociation might be observed. There are both diffuse and sharp observed levels above the ICl predissociation limit, according to Brown and Gibson. These levels do not fit the simple scheme of the $^3\Pi_{O^+}$ level. It might be possible that the levels are actually a set of vibronic states resulting from mixing of the two electronic levels under the influence of the potential and nuclear kinetic energy operators. If this were the case, the levels could hypothetically be determined by solution of a secular equation analogous to that of Eq. (5). At present, however, this seems to be an unduly difficult task.

One final remark might be made regarding the magnitude of the matrix element (6). The larger is this term,

¹⁶ F. H. Crawford and T. Jorgensen, *Phys. Rev.* **47**, 358, 932 (1935); *ibid.* **49**, 745 (1936).

¹⁷ R. S. Mulliken, *Phys. Rev.* **50**, 1035 (1936).

¹⁸ E. J. Rosenbaum, *J. Chem. Phys.* **6**, 16 (1938).

¹⁹ G. Büttenbender and G. Herzberg, *Ann. Phys.* **21**, 577 (1935).

²⁰ W. G. Brown and G. E. Gibson, *Phys. Rev.* **40**, 529 (1932).

the more probable the violation of the noncrossing rule. The value of the term becomes large primarily when the peaked function $d\omega/dR$ becomes narrow with respect to the wavelength of the vibrational function f . The factor $d\omega/dR$ itself tends to a δ function normalized to $\pi/2$ as its half-width becomes zero. Moreover the half-width depends primarily on the overlap of the two approximate state functions ψ_1 and ψ_2 , the ionic and atomic functions, in the region where ω is changing. Because the potential curve of ψ_1 is ionic, it shows an attractive slope of considerable magnitude at distances where covalent potential curves are still horizontal. Consequently the ionic ψ_1 curve intersects the ψ_2 curve at an internuclear separation very large compared with those leading to predissociations like that of the C state of N_2 . (This itself is a type 1(c) predissociation in which the two curves involved intersect at a distance of over $4A$.¹⁹) At such large separations (see Table I), the overlap of ψ_1 and ψ_2 is extremely small so that $d\omega/dR$ is large over only a very small range of internuclear separation. Predissociations like those of nitrogen or iodine chloride are due to crossovers at separations even less than that of R_x for sodium iodide. As a result, one might expect the nuclear vibration factor f to play a more important part in predissociations of covalent molecules like N_2 than it does for alkali halides. In fact, it may well be that the influence of the f factor leads to the return of bound states above the energy at the crossing point, as in ICl . At energies corresponding to high vibrational states, the f term may well have a wavelength short enough to diminish the integral (6) significantly in a case like that of iodine chloride. Such influence is much more likely to occur for covalent molecules for which ω changes slowly than for ionic molecules, for which at a large internuclear distance, the electronic wave function must change rapidly if the noncrossing rule is to apply.

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APPENDIX. THE $4s-5p\sigma$ OVERLAP APPROXIMATION

We seek to approximate the overlap integral $S(4s,5p\sigma)$ between two widely separated Slater orbitals. Following the notation of reference 14, we let

$$\begin{aligned} a_0 &= \text{the Bohr radius,} \\ Z_A &= \text{effective nuclear charge of nucleus } A, \\ n^* &= \text{effective quantum number (3.7 for } n=4, 4 \text{ for } n=5), \\ \mu &= Z/n^*, \\ p &= \frac{1}{2}(R/a_0)(\mu_A + \mu_B), \\ t &= \mu_A - \mu_B / \mu_A + \mu_B, \text{ and} \\ \rho_A &= \mu_A R / a_0. \end{aligned}$$

The integral may be expressed in elliptical coordinates with

$$\xi = (r_1 + r_2) / R$$

and

$$\eta = (r_1 - r_2) / R.$$

So expressed, the overlap becomes

$$S(4s,5p\sigma; R) = \frac{\sqrt{3}}{2} \frac{\rho_k^{4.2} \rho_l^{9/2}}{(\Gamma(8.4)\Gamma(9))^{1/2}} \int_{-1}^1 \int_1^\infty (\xi^2 - \eta^2)^3 \times (\xi\eta - 1)e^{-p(\xi+t\eta)} (\xi+\eta)^{0.7} d\xi d\eta. \quad (A1)$$

The term $(\xi+\eta)^{0.7}$ is expanded in a binomial series and substituted in (A1). When the integration over η is carried out, a series in ξ results; only the eight terms with positive powers of ξ are significant. The coefficients contain up to eight of the well-known $B_n(pt)$ integrals.¹⁴

For very large distances, so that $pt \geq 1.3$, the overlap formula may be given approximately as

$$S(4s,5p\sigma) = 1.211 \times 10^{-4} p^{5.7} t^{-2} (1+t)^{4.2} (1-t)^{9/2} \times e^{-p(1+t)} \left[1.62 + \frac{7.64}{pt} + \frac{1.13}{p} + \frac{5.35}{p^2 t} \right]. \quad (A2)$$

The derivation is given by a similar formula,

$$\begin{aligned} R \frac{dS}{dR} &= 1.211 \times 10^{-4} p^{5.7} t^{-2} (1+t)^{4.2} (1-t)^{9/2} e^{-p(1+t)} \\ &\times \left[\frac{12.99}{t} + 0.46 - 1.62p(1+t) \right. \\ &\quad \left. + \frac{30.56}{pt} + \frac{5.311}{t} - 1.13t + \frac{25.14}{p^2 t} \right]. \quad (A3) \end{aligned}$$

The values of S and RdS/dR at the crossing points are given in Table II.