

Spectra of the Alkali Halides. III. Electronic Spectra of Lithium Chloride, Lithium Bromide, and Lithium Iodide

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The ultraviolet absorption spectra of the molecules LiCl, LiBr, and LiI have been observed in the quartz region. These spectra, which appear as continua with associated diffuse bands, have been interpreted as arising from excitations to two excited states of the molecules. The symmetries and potential curves for these states are discussed.

I. INTRODUCTION

RECENTLY, investigations of the microwave and infrared spectra^{1,2} of several alkali halide molecules have given a rather detailed picture of the lowest electronic states of these molecules, particularly for the regions of their equilibrium internuclear separations. This note is an attempt to study the ultraviolet spectra of several lithium halides and thereby to examine their excitations to higher electronic states. It is assumed that the ground states of the alkali halides are described accurately by an ionic model; with this hypothesis, the lowest potential energy curves may be constructed from the data of references 1 and 2 above. The observed electronic spectra correspond then to excitations from this curve to higher states. The spectra reported here, as well as those reported for other alkali halide molecules,^{3,4} appear as continua with associated diffuse bands. These results are generally interpreted⁵⁻⁷ as indicating that the upper states of the molecule are nonbonding and have the character of the two atoms. The spectra, therefore, arise from an electron transfer process in which the molecule makes a transition from a strongly bound and almost totally ionic state to a nonionic repulsive state.

II. EXPERIMENTAL

The apparatus is a standard one for high temperature spectroscopy. (See, for example, reference 3 or 4.) The salt samples are heated in a tube furnace; the furnace core itself is a ten-inch alumina tube wound with Kanthal A-1 resistance wire. The samples are placed in the center of a steel tube, five feet long and two inches in diameter, which runs through the furnace. The sample tube is filled with argon to inhibit salt condensation on the quartz windows sealed onto the ends of the tube. The furnace may be operated at temperatures up to about 1300°C.

¹ Honig, Mandel, Stitch, and Townes, *Phys. Rev.* **96**, 629 (1954).

² W. Klemperer and S. A. Rice, *J. Chem. Phys.* **26**, 618 (1957).

³ H. Levi, Doctoral dissertation, Berlin, 1934.

⁴ R. F. Barrow and A. D. Caunt, *Proc. Roy. Soc. (London)* **A219**, 120 (1953).

⁵ W. Finkelnburg, *Kontinuierliche Spektren* (Julius Springer Verlag, Berlin, 1938), p. 173 ff.

⁶ R. S. Mulliken, *Phys. Rev.* **51**, 310 (1937).

⁷ G. Herzberg, *The Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 387 ff.

A medium Bausch and Lomb quartz prism spectrograph is used; in the region of interest (2500–4500 Å), the dispersion is 10–15 Å/mm. Photographs have been taken with slit widths varying between 40 and 160 microns. The observed bands are of the order of 50 Å wide.

Spectrograms are taken on Eastman Kodak Royal Pan film, which has more desirable characteristics for this work than the Eastman O or F type spectroscopic plates. Films are developed in Eastman DK-50 for four to five minutes. The light source selected for the 3000–4500 Å region is a G-E 1000-watt tungsten filament projection bulb. A Hanovia high pressure xenon arc, model 10-C-1, is used to reach 2600 Å.

Because the bands in the spectra are so diffuse, several measurements are made of each band in order to minimize errors in determining their location. The observed bands are given in Table I, together with their separations and vibrational assignments.

III. DISCUSSION

The lowest electronic states of the lithium halides show no net orbital nor spin angular momentum and may be denoted as ${}^1\Sigma^+$ or 0^+ in the notation appropriate to Hund's coupling cases (a) and (c), respectively. In the region of their equilibrium internuclear distances, the potential energy curves of these states are given

TABLE I. Observed bands of LiCl, LiBr, and LiI.

LiCl v''	$(\omega_e = 661 \text{ cm}^{-1})$		LiI v''	$(\omega_e = 501 \text{ cm}^{-1})$	
	Frequency	Difference		Frequency	Difference
7	35 642 cm^{-1}		1	29 146 cm^{-1}	
8	35 032	610 cm^{-1}	2	28 524	622 cm^{-1}
9	34 482 (?)	550	3	27 981	543
					572
			4	27 409	486
					535
5	31 560	542	5	26 923	508
6	31 018	551	6	26 388	557
7	30 467	588	7	25 880	457
8	29 879	437	8	25 323	359
9	29 442 (?)		9	24 866	
			10	24 507 (?)	

remarkably well by an equation of the form,^{1,8}

$$W = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{c}{r^6} - \frac{2e^2\alpha_1\alpha_2}{r^7} + Ae^{-r/\rho}. \quad (1)$$

In this equation, W is the potential energy, e the electronic charge, α_1 and α_2 the polarizabilities of the lithium and halide ions, r the internuclear distance, c the van der Waals constant, and A and ρ adjustable parameters to fit the repulsive part of the curve. This formula was first suggested by Born and Mayer⁹ who applied it to ionic crystals. Rittner, as described in reference 8, applied the equation to the alkali halide molecules. For large nuclear separations, where the systems are described best in terms of the separated atom functions, the energy level corresponding to Li^+ and X^- , where X^- is the halide ion, lies above that corresponding to the neutral atoms. Consequently the Rittner model will be valid only for the very strongly bound region. Figures 1 and 2 show the behavior of this approximation for the ground states of LiI and LiBr in such regions. According to the noncrossing rule, the ground

TABLE II. Energy levels of isolated atoms (energies relative to ground-state atoms, in eV).

$X =$	Cl	Br	I
$\text{Li}(^2S_1) + X(^2P_1)$	0	0	0
$\text{Li}(^2S_1) + X(^2P_2)$	0.109 ^a	0.457 ^a	0.943 ^a
$\text{Li}(^2P) + X(^2P_1)$	1.848 ^a	1.848 ^a	1.848 ^a
$\text{Li}^+(^1S) + X^-(^1S)$	1.662 ^{a,b}	1.896 ^{a,c}	2.25 ^{a,d}

^a "Atomic energy levels". Circular 467 (Department of Commerce, National Bureau of Standards, Washington, D. C.)

^b K. J. McCallum and J. E. Mayer, *J. Chem. Phys.* **11**, 55 (1943).

^c P. M. Doty and J. E. Mayer, *J. Chem. Phys.* **12**, 323 (1944).

^d P. P. Sutton and J. E. Mayer, *J. Chem. Phys.* **3**, 20 (1935).

state must change character, from ionic to atomic, as the nuclei move out to the region where the attractive Coulomb curve crosses the energy level of the ground-state atoms (see Table II).

The ground-state atoms can combine adiabatically to give several excited states, in addition to the molecular ground state; these are best described by angular momentum coupling of the type of Hund's case (c), because of the large spin-orbit coupling in the halogens and the weak valence forces in the molecules. That is, orbital and spin angular momenta about the internuclear axis, Λ and Σ , respectively, are not good quantum numbers although Ω , the total angular momentum about the figure axis is a constant of the motion. In toto, five states arise from $\text{Li}(^2S) + X(^2P_3/2)$, corresponding to $\Omega = 2, 1, 1, 0$, and 0 . The last two may be classified further according to their behavior upon reflection in a plane containing the internuclear axis; the symmetric function is called 0^+ and is the

⁸ E. S. Rittner, *J. Chem. Phys.* **19**, 1030 (1951).

⁹ M. Born and J. E. Mayer, *Z. Physik* **75**, 1 (1932).

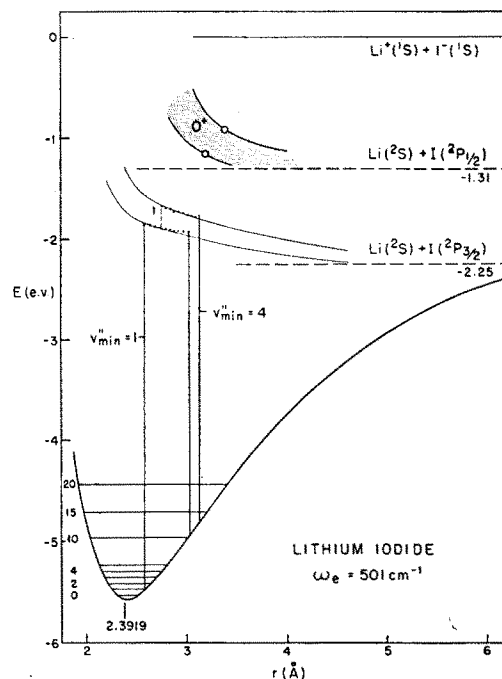


FIG. 1. The electronic states and observed transitions of lithium iodide.

molecular ground-state function, while the other is antisymmetric and is labeled 0^- .

In the next set of levels, derived from $\text{Li}(^2S) + X(^2P_1)$, there are three states, characterized as 0^+ , 0^- , and 1 . Corresponding to the dissociation limit $\text{Li}(^2P) + X(^2P_1)$, there are many possible states, with values of Ω from

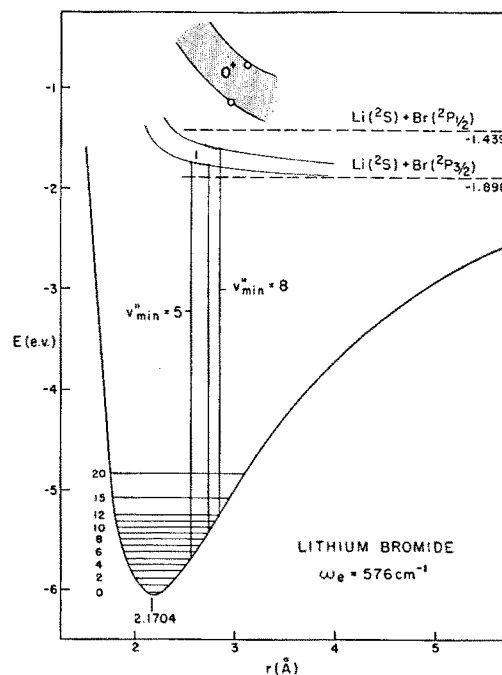


FIG. 2. The electronic states and observed transitions of lithium bromide.

3 to 0. The limit $\text{Li}^+(^1S)+X^-(^1S)$ can give rise only to a 0^+ state.

The only electric dipole transitions allowed from the 0^+ ground state are those to 0^+ and 1 states. The former are essentially parallel type charge transfer processes and should be quite intense. Transitions to 1 states have transition dipole moments perpendicular to the internuclear axis and are therefore weaker by a factor of 10^{-2} to 10^{-3} than the $0^+ \rightarrow 0^+$ processes.

The lower excited states of these molecules would be, in general, nonbonding. The $0^+ \rightarrow 0^+$ excitation, for example, may be looked upon as excitation of an electron from a bonding σ orbital located near the halogen to an antibonding σ orbital located near the lithium. Again, the lowest 1 state has some of the character of a $^3\Sigma$ state analogous to the antibonding state of hydrogen, and some of the character of a $^1\Pi$ state in which there is very little overlap of the electron clouds. (See, for example, reference 6.) On this basis, the first excited 0^+ state would be repulsive and the lowest 1 state, while still repulsive, could be rather flat. This is also in harmony with the fact that the 1 state is the lowest of its symmetry type and therefore is "pushed down" by all the higher states with $\Omega=1$.

Repulsive states give rise only to continuous spectra. If, however, one of the states involved in a transition is attractive and the other is repulsive but almost flat, the absorption spectrum will show so-called fluctuation bands. That is, instead of a smooth continuum, the spectrum will appear as a series of broad, diffuse bands which are actually fluctuations in the intensity of the continuous absorption. These arise from the fact that an oscillator may be found most probably in the vicinity of its turning points, and by the Franck-Condon principle, will be excited vertically upward to the excited electronic state. The fluctuation bands, therefore, must be separated by an energy difference equal to the separation of the vibrational levels of the unexcited molecule, plus a small amount due to the slope of the repulsive state. If the upper state is too repulsive, the bands will overlap and broaden, so that only a smooth continuum will appear in the spectrum. This is, in fact, what one would expect over the left-hand turning points of the unexcited molecule, corresponding to short internuclear distances; only transitions from the right-hand turning points should give rise to fluctuation bands.

From Table I, it is apparent that the bands observed in the spectra of the lithium halides are separated by an amount roughly equal to the observed vibrational frequency. The upper state of the transition may be located simply by an assignment of the vibrational states from which the bands arise. On the basis of the temperatures at which the bands were observed and of the flatness of the upper state, the assignment is made for LiI of $1 \leq v''_{\min} \leq 4$, where v''_{\min} is the vibrational quantum number of the lowest vibrational level associ-

ated with an observed band. The position of the excited state would lie between the limits indicated by the dots (observed transitions, shown for upper and lower limits of the assignment) in Fig. 1.

The continuum is observed even when the partial pressure of salt vapor is reduced from *ca* 10 mm to *ca* 0.1 mm; this implies that the continuum has an intensity 100 to 1000 times that of the bands, if they are different transitions. A computation of the relative populations of vibrational states permits a rough assignment of the vibrational state responsible for the red limit of the continuum at any given temperature. Even then, however, it may be very difficult to locate the curve of the continuum because of the approximations involved in the Franck-Condon principle.¹⁰

As mentioned previously, the transition from the ground state to the first excited 0^+ state should be about 100 times more intense than the ground to $\Omega=1$ transition. It is suggested that the bands are in fact due to the latter transition and the continuum to the former. Crude estimates of the position of the continua are shown in the figures.

A piece of supporting evidence arises from the comparison of the spectra of these three halides. As the spin-orbit coupling of the halogen atoms decreases, going from iodine to chlorine, the two lowest dissociation limits come closer together. Under such circumstances, the intense continuum should mask more bands in LiBr than in LiI, and still more in LiCl. This is indeed what is observed. It is in fact possible to estimate how many bands of LiBr and LiCl are hidden by using data on the iodide to make a vibrational assignment of the bands in the spectra of the lighter halides. For the bromide, with a temperature of about 1500° K, it is estimated that v_{\max}'' lies between 9 and 12, so that the shortest wavelength band corresponds to v'' between 5 and 8. These limits are shown in Fig. 2. In the case of lithium chloride, with T between 1500 and 1700° K, the limits on v_{\max}'' would again be 9 and 12, so that the highest energy transition would arise from v'' between 7 and 10.

One further observation might be made at this point. The difference between the separations of the observed bands and the vibrational frequency found from the infrared spectrum is positive for LiI, slightly less than zero for LiBr (about -15 cm^{-1} , within experimental error), and quite negative for LiCl. This is explained by noting that the only vibrational states giving rise to observed bands for LiCl and LiBr are relatively high and therefore should show large anharmonic effects. This should be especially important for the chloride, where anharmonicity should be largest. Consequently the first allowed excited state may be of almost exactly the same form for all three salts and still give rise to this apparent anomaly.

¹⁰ Coolidge, James, and Present, *J. Chem. Phys.* 4, 193 (1936).