

Resonances in photodetachment of sodium halide negative ions

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The cross sections for photodetachment of the alkali halide negative ions NaCl^- , NaBr^- , and NaI^- have been measured in the photon energy range 2.0–2.3 eV. In this energy range, well above the photodetachment threshold at approximately 0.6 eV, the only processes energetically accessible are photodetachment to produce the ground electronic state neutral alkali halide, and photodissociation. For each of the sodium halides, we observe a single isolated resonance in the cross section, occurring approximately 160 cm^{-1} to the high energy side of the neutral sodium atom $3s$ – $3p$ energy difference. This resonance is interpreted as autodetachment of a $^2\Pi$ state of the negative ion imbedded in the photodetachment continuum. The $X^2\Sigma$ – $A^2\Pi$ energy difference in NaX^- is almost completely halide independent, providing strong support for the qualitative picture of the negative ion as being composed of a neutral sodium atom adjacent to a closed shell halide ion. Qualitative fits of the experimental data utilizing the Fano formalism indicate that the lifetime of the autodetaching state is on the order of 10^{-12} sec and that the shape of the potential well for the $^2\Pi$ state is virtually identical to that of the negative ion ground state.

I. INTRODUCTION

Since the introduction by Fano¹ of a formalism describing the interaction of a discrete level with an adjacent continuum, and the observations of resonances in photoionization² and the discovery of resonances in electron scattering,^{3,4} this subject has played an important role in atomic and molecular physics. The electron scattering resonances are interpreted in terms of temporary negative ion states, and are frequently found in systems for which no stable negative ion exists. Recently, however, strong resonances have been found in photodetachment of atomic alkali negative ions well above the photodetachment threshold^{5,6} and in molecular negative ions⁷ near the photodetachment threshold.

For both applied⁸ and basic reasons, there has been considerable interest in electron scattering from strongly polar molecules and in the bound states of negative ions formed from a highly polar parent. An investigation of the electron affinity of LiCl ⁹ indicated clearly that the simple model of an electron bound in the field of a permanent dipole is inappropriate to describe the ground electronic state of alkali halide negative ions. Jordan and coworkers^{10–13} have made it clear that a more appropriate zero order model is that of a neutral alkali next to a halide ion. To investigate this picture further, we have studied the photodetachment of the alkali halide negative ions NaCl^- , NaBr^- , NaI^- and LiCl^- at photon energies well above the photodetachment threshold (~ 0.6 eV), in the vicinity of the resonance transition energy difference in the appropriate alkali neutral species. The three sodium halide cross sections show a strong resonance feature very close

to the $3s$ – $3p$ energy difference in neutral sodium; the LiCl^- cross section shows no such structure.

II. EXPERIMENTAL

The tunable laser photodetachment apparatus has been previously described in detail.^{5b,14} Briefly, the appropriate alkali halide salt is vaporized into a low pressure hot cathode discharge. The desired alkali halide negative ion is apparently produced by dissociative electron attachment to the neutral dimer and is a minor component of the negative ion flux, the primary one being the atomic halide ion produced by dissociative attachment to the monomer. Negative ions are extracted from the ion source, focused into a beam and mass selected through a 90° sector magnet with a resolution $m/\Delta m \sim 40$. The mass selected 1 nA beam at an energy of 2000 eV is crossed with the intracavity radiation of an Ar^+ -pumped jet stream dye laser. The commercial dye laser is used intracavity by replacing the 3% transmitting flat output mirror with a 1 m radius of curvature high reflectivity back mirror, extending the length of the laser cavity by 1 m to include the ion beam apparatus. Typical circulating photon fluxes are approximately 15 W with wavelength resolution between 3 and 0.3 Å, depending upon the experiment.

The ion and laser beams cross at 90° in an interaction region consisting of a cylindrical can with appropriate aperture holes for the beams and for the extraction of the photodetached electrons. A weak extraction field (~ 1 V/m) is applied which draws out slow electrons (< 50 meV) from the interaction region after which they are detected by a channeltron electron multiplier and counted; faster electrons are largely unaffected by this field and primarily strike the walls of the interaction region where they are absorbed by a gold-black metal surface. The heavy particles, negative ions, and the neutrals resulting from the photodetachment process travel through the interaction region to an electrostatic separator which segregates the various heavy particle

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components. The undeflected neutral molecules (at 2 keV kinetic energy), are detected by secondary electron emission and counted using a continuous dynode electron multiplier. The negative ions are deflected by the electrostatic separator into a Faraday cup which serves as a beam monitor. The electron channeltron, the neutral molecule electron multiplier and the negative ion Faraday cup are all interfaced to a PDP-8/E computer. The data acquisition system also monitors the laser flux, controls the tunable laser frequency, and makes appropriate background corrections to the detected signals in order to obtain relative photodetachment cross sections.

This experimental arrangement thus results in the measurement of two cross sections: a total photodestruction cross section, which is the cross section for production of neutral particles, and a slow electron production cross section obtained from the electron detector. At the photon energies employed in this study, only the ground electronic state of the neutral alkali halide is energetically accessible, and the slow electron cross section is hence a cross section for production of ground electronic state alkali halide neutrals in very high vibrational levels (typically $v \sim 50$). Such data were obtained for NaBr^- , NaCl^- and NaI^- in the wavelength region 6200–5700 Å; for LiCl^- , the wavelength range 7000–5500 Å was studied. In each case the wavelength of the neutral alkali resonance transition (~ 5890 Å for Na and ~ 6710 Å for Li) was included in the data set. We were not able to produce negative ion beams for any of the alkali fluorides.

III. RESULTS AND DISCUSSION

Figure 1 shows the total photodestruction cross section and the threshold electron production cross section for NaBr^- in the wavelength region 6200–5700 Å, far

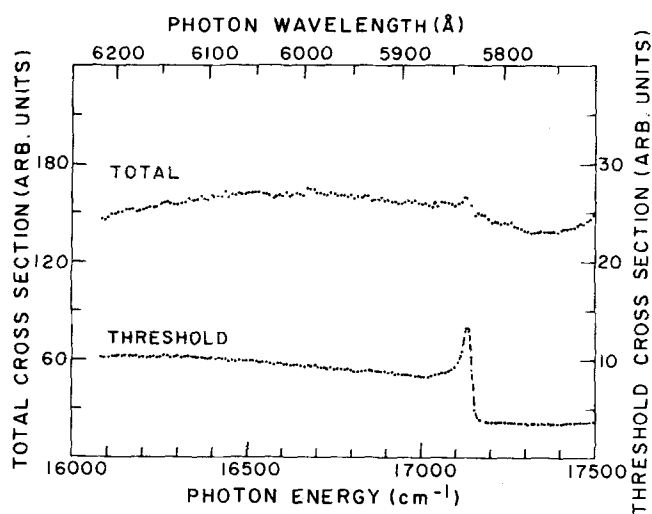


FIG. 1. NaBr^- low resolution total and threshold photodetachment cross sections. These are representative of all the NaX^- systems studied. The total cross sections are obtained from the neutral channel and may contain contributions for photodissociation. The threshold cross section represents the production of slow electrons by detachment into high lying vibrational states of the neutral.

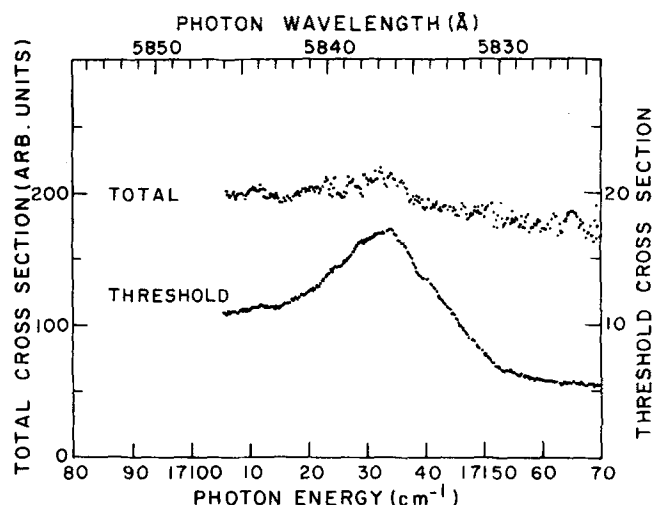


FIG. 2. Expanded view of the NaCl^- photodetachment resonance. Note that the threshold resonance is $\sim 1\%$ of the total cross section.

above the photodetachment threshold. Since only the ground electronic state of NaBr is energetically accessible in this wavelength region, the threshold electron cross section is in fact a cross section for production of NaBr in vibrational levels nearly 1.5 eV above the bottom of the ground state well, namely $v \cong 50$. The most striking feature of these data is the single peak which occurs in the threshold electron cross section near 5840 Å. One should note the difference in scales for the two curves of Fig. 1; the sharp peak in the high V cross section produces only a few percent feature, barely noticeable, in the total cross section. As indicated below, the data of Fig. 1 are characteristic of all of the sodium halides.

Each of the three sodium halides studied shows a single isolated peak in the threshold electron production cross section at essentially the same photon energy. The approximate peak centers are 17132, 17129, and 17124 cm^{-1} for NaCl^- , NaBr^- , and NaI^- , respectively. The principal difference in these data is that the relative importance of the threshold electron resonance in the total cross section increases substantially as the halide mass increases, increasing from 1% of the total cross section for NaCl^- to 25% for NaI^- . Higher resolution views of these resonances for all three sodium halide negative ions are shown in Figs. 2–4. The resonances are typically 20 cm^{-1} wide, with a substructure in the threshold electron cross section which is real and reproducible.

It is apparent that these three resonances are strikingly similar: (1) They occur at essentially the same photon energy, 160 cm^{-1} above of the sodium resonance transition. (2) The threshold cross section is substantially smaller above the resonance than below it. (3) The width of each resonance is approximately the same, 20 cm^{-1} , and (4) each of the resonances shows substructure, being most clearly visible in the NaI^- data and barely detectable in the NaCl^- cross section. These results suggest strongly that the origin of the resonance is the same in each of these systems, the

location of the resonance being related to Na, and the coupling to the detachment continuum being related to the halide.

Qualitatively it is reasonable that one is forced to think in terms of an atomic sodium property for the location of the resonance. Dipole moments of the neutral sodium halide when corrected for polarizability effects show that the salts are almost 100% ionic at their equilibrium separation. The Na^+X^- nature of the neutral implies that the available orbital for the additional electron forming the anion is the sodium 3s orbital; thus a primitive model for the negative ion is a 3s neutral sodium atom adjacent to a $np^6 \text{X}^-$ ion. Excitations of NaX^- , then, are similar in character and energy to atomic sodium excitations, the first of which would be $3s \rightarrow 3p$, giving rise to $^2\Sigma$ and $^2\Pi_{1/2,3/2}$ excited states of NaX^- . The $^2\Pi$ states arise from excitation to a p orbital perpendicular to the internuclear axis and hence are not substantially perturbed by the presence of the halide. The $^2\Sigma$ state arises from a p orbital oriented along the internuclear axis and probably occurs at energies above the sodium resonance transition with a location which is halide dependent. These negative ion excited states lie in the $(\text{NaX} + e)$ continuum; they must be rather weakly coupled to the detachment continuum in order to be observed as resonances.

There is only one resonance observed for the sodium halide negative ions in the energy region around the neutral sodium resonance transition. We tentatively assign resonance to be due to the $A^2\Pi$ autoionizing state of NaX^- . Based on previous experience,¹⁵ we expect the NaX^- ions to be produced in a variety of vibrational states corresponding to a temperature near 1000 K. Thus one would expect to see a series of resonances, corresponding to $\Delta v = 0, \pm 1, \pm 2$, etc., between various levels of the negative ion and vibrational levels of the $^2\Pi$ state, the intensities being determined by Franck-Condon factors and initial populations. As vibrational frequencies are approximately 300 cm^{-1} , it is clear that we are not observing such sequences but only Δv

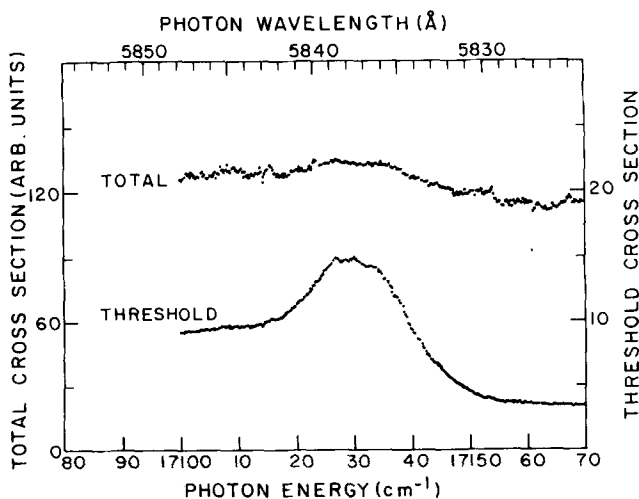


FIG. 3. Expanded view of the NaBr^- photodetachment resonance. Note that the threshold resonance is $\sim 5\%$ of the total cross section.

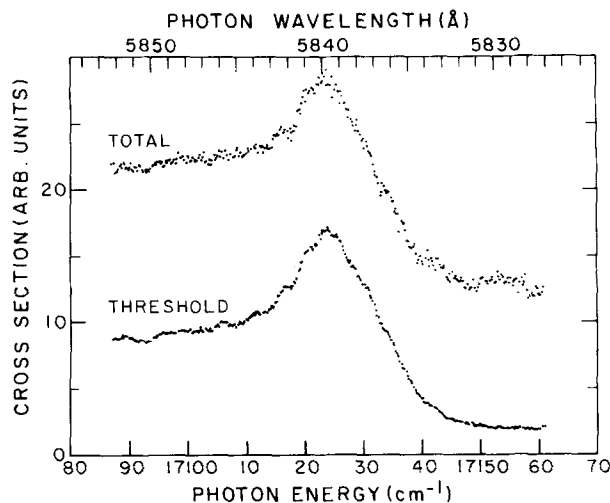


FIG. 4. Expanded view of the NaI^- photodetachment resonance. Note that both the total and threshold cross sections are on the same scale and the threshold resonance is $\sim 25\%$ of the total cross section.

$= 0$ transitions. The lack of detection of other sequence bands puts severe constraints on the difference in the equilibrium internuclear separation between the two negative ion states. If we assume (conservatively) that our signal-to-noise level is such that we would have detected a sequence band with an intensity one tenth of that observed in the resonance, a simple harmonic oscillator Franck-Condon analysis implies that $|\langle r_e(A^2\Pi) - r_e(X^2\Sigma) \rangle| < 0.04 \text{ \AA}$ for all of the sodium halides. We have assumed that $\omega_e(\text{NaCl}^-X^2\Sigma) = 290 \text{ cm}^{-1}$,¹² and taken this number for NaBr^- and NaI^- to be about 80% of that in the corresponding neutral.

This picture of NaX^- as a neutral sodium atom adjacent to X^- is actually a simplification of a model of alkali halide negative ions arrived at by Jordan *et al.* based on *ab initio* calculations and considerations of the bending of an electron in the field of a molecular dipole.¹⁰⁻¹² The *ab initio* calculations for LiCl^- , for example,¹⁰ show that the extra electron occupies a predominantly nonbonding orbital which has the greatest electron density behind the lithium atom. Moreover, Jordan and co-workers find a nearly linear relationship between the dipole moment of the neutral molecule and its electron affinity for a series of lithium compounds and independently for a series of sodium compounds.^{12,13} This finding strongly suggests that the bonding of the electron to the neutral alkali halide is rather insensitive to the detailed electronic structure of the negative end of the molecule.

The resonances of Figs. 1-4 show substructure with individual widths of $3-5 \text{ cm}^{-1}$. This width is hence an upper limit to the homogeneous width of the individual resonances, implying a lifetime of the autoionizing state greater than 10^{-12} sec . The overall 20 cm^{-1} width of the resonance must include all sequence bands ($\Delta v = 0; v = 0, 1, 2, 3, \dots$), individual rotational transitions, and the spin orbit splitting of the $^2\Pi$ state into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. In order to accommodate this result, it is necessary that the vibrational frequency of the upper and lower

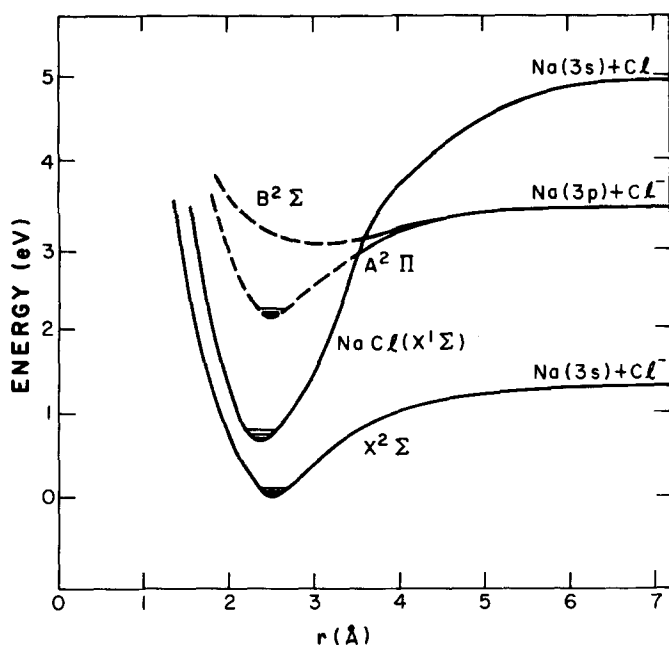


FIG. 5. Sketch of the four lowest molecular potential curves for NaCl and NaCl⁻. The dashed lines represent autodetaching states of the negative ion. See text for details.

state differ by no more than 10 cm^{-1} and, if both spin orbit components participate in the resonance, that the spin orbit splitting be no more than 15 cm^{-1} . The net result is that there must be at least one ${}^2\Pi$ autoionizing state for which both r_e and ω_e are virtually identical to those quantities in the negative ion ground state. The term energy of this state is 1% greater than the sodium $3s-3p$ resonance energy; potential energy curves embodying this information are shown in Fig. 5. The electron affinity of NaCl has been taken to be 0.65 eV ^{12,13} and $r_e(\text{NaCl}^-X^2\Sigma)$ to be¹² 2.51 \AA . The location of the ${}^2\Pi$ state is in complete accord with the SCF calculations of Stevens¹⁶ on LiF⁻, which shows the $A^2\Pi$ state parallel to the $X^2\Sigma$ state and separated from it by the ${}^2P-{}^2S$ of the lithium atom. The $B^2\Sigma$ state is somewhat more troublesome. In order to obtain Σ overall symmetry, the sodium p orbital is oriented along the internuclear axis; since the Cl⁻ is a closed-shell system the interaction is expected to be repulsive at short distances and hence the $B^2\Sigma$ state will be repulsive. This is the picture that Jordan and Luken¹⁰ present in their sketch of the LiCl⁻ state.⁵ However Stevens,¹⁶ in his calculation of the $B^2\Sigma$ state of LiF⁻, finds this state to be attractive and only 0.3 eV above the $A^2\Pi$ state at the equilibrium separation. No attempt has been made to calculate the lifetimes of any of these states in the autodetaching region. While we find evidence for only one state, the $A^2\Pi$, our experiment probes only a rather small energy region; a $0.3 \text{ eV } B^2\Sigma-A^2\Pi$ splitting would put the $B^2\Sigma$ state out of the range of our study.

Based upon this simple model, we expected to find a similar resonance in the photodetachment of LiCl⁻, slightly to the high energy side of the atomic lithium resonance transition. No such feature was found and we have no convincing explanation for this result. The

data of Figs. 2-4 also indicate that the strength of the resonance dramatically increases for the heavier halides; an explanation of this result is not incorporated in the model. The qualitative features of the resonance, including the substructure, can be fitted using the Fano picture¹ of a single discrete state embedded in a single continuum. The actual system is of course far more complicated, in that there are many discrete states—vibration/rotation/spin-orbit of the $A^2\Pi$ —embedded in many continua; each continuum begins on a specific vibration/rotation level of the $X^1\Sigma$ neutral molecule. Experimentally, we see that the resonances predominantly manifest themselves as an increase in the production of low-energy electrons. This result means that of all possible continua, the discrete states couple strongly to very few—those whose limit they are near degenerate with. The reason for this result is not clear at this time.

Various calculations and experiments have been performed on systems isoelectronic with the alkali halide negative ions. Pascale and Vandephanque¹⁷ have carried out semiempirical calculations on alkali-rare gas systems. Here the $X^2\Sigma$ states are, of course, repulsive, since the van der Waals attraction is much weaker than the bonding of an electron to a polarizable dipolar molecule. The $A^2\Pi$ states are attractive but only weakly so, the well depth being only a few tenths of an eV even in the Cs-Xe case. The $B^2\Sigma$ states are all repulsive but show metastable wells at short distances. Gallagher and coworkers¹⁸⁻²¹ have mapped large portions of the alkali-rare gas potentials by monitoring the emission profiles of the alkali lines broadened by collisions with rare gases. In all cases they find the $A^2\Pi$ state to be slightly bonding and the $B^2\Sigma$ states, where investigated, to be repulsive. Bender²² has completed *ab initio* calculations on another isoelectronic series, the alkaline earth monohalides. It appears that the qualitative nature of the $A^2\Pi$ and $B^2\Sigma$ states are again bonding and repulsive respectively. It is quite striking that experimentally the $A^2\Pi-X^2\Sigma$ energy separation in the alkaline earth monohalides is similarly insensitive to the identity of the halide: for example in MgCl and MgBr (isoelectronic with NaCl⁻ and NaBr⁻) these energies are within 3% of each other. It is also possible that these resonances would show up in a very high resolution investigation of electron-alkalides inelastic scattering cross sections. Collins and Norcross²³ have calculated such cross sections in the body-fixed frame using close coupling calculations, employing the full static potential plus the local energy dependent exchange model potential. They find resonances in the cross sections of both Σ and Π symmetry for LiF, NaF, NaCl, but not for LiCl. These resonances are very broad, 0.1 eV for the Σ symmetry and 1 eV for the Π , and it is not at all obvious that our measurements and their calculations are concerned with the same systems.

It should be emphasized that, whatever the origin of the resonances, these data imply there is a strong enhancement of the final population of a high vibrational state of the neutral end product. This is especially true of the NaI case where, from the data of Fig. 3, we see that the resonance in the slow electron channel

results in a 25% enhancement of the total photodetachment cross section. Taking the electron affinity of NaI to be 0.70 eV, at the peak of the resonance 75% of the NaI ends up in an unknown vibrational distribution and roughly 25% is in a very high vibrational level, approximately $v = 55$!

IV. CONCLUSIONS

Cross sections for photodestruction of sodium halide negative ions have been measured in an energy regime encompassing the atomic sodium resonance transition. In this energy regime, well above the photodetachment threshold, a single sharp resonance is seen in the photodetachment cross section, which gives rise to highly vibrationally excited ground state alkali halide neutrals. The energy of this resonance is essentially halide invariant, but the strength of the resonance increases dramatically as halides become heavier. A simple model is invoked which rationalizes most but not all of these results.

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