

BINDING OF AN ELECTRON BY THE FIELD OF A MOLECULAR DIPOLE – LiCl⁻

J.L. CARLSTEN, J.R. PETERSON*

Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80302, USA

and

W.C. LINEBERGER**

Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards and Department of Chemistry, University of Colorado, Boulder, Colorado 80302, USA

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We present direct experimental evidence for the binding of an electron by the dipole moment of a neutral molecule. The photoelectron spectrum of LiCl was obtained and analyzed to determine that the binding energy of the electron in the LiCl⁻ ion is (0.61 ± 0.02) eV. This result is an order of magnitude smaller than the predictions of the fixed dipole theoretical model, but is consistent with a recent calculation, which allows for distortion of the dipolar core.

1. Introduction

The binding of an electron by a dipole field of a neutral particle has attracted considerable attention over the past years. An initial theoretical study [1] dealt with the interaction of negative mesons with hydrogen. These studies indicated a critical dipole moment of $0.639 ea_0$ formed by the proton and negative meson was needed to bind the electron. Later Wallis et al. [2] calculated the energy levels of an electron in the field of a rigid dipole. A number of researchers [3–5] then rediscovered that the minimum dipole moment needed to bind the electron was $0.639 ea_0$. Subsequently Crawford [6] showed that, for a rigid dipole with a moment greater than $0.639 ea_0$, an infinite number of bound states exist. Recently rotational effects have been shown to raise the minimum dipole moment necessary to bind an electron and also to reduce the number of bound states [7–9].

Experimental evidence for the binding of an elec-

tron by the dipole field of a polar molecule has been indirect at best [10]. Electron swarm data [11,12] indicate drastic changes in the electron drift velocity in polar gases when the dipole moment becomes greater than $0.639 ea_0$. Such behavior has been interpreted as due to the formation of temporary bound negative ions as the electron drifts through the polar gas. Scattering experiments [13] of electrons by alkali-halides have been compared with calculations using the first Born approximation, and a point-dipole model. These experiments indicate that the absolute total cross sections are considerably less than those predicted using the first Born approximation. Recent close coupling calculations by Allison [14] have improved the agreement with experiment for momentum transfer cross sections.

Since LiCl is a closed shell molecule, binding of an extra electron is not obviously expected. However, LiCl has a large dipole moment which is capable of binding the extra electron. We have produced LiCl⁻, determined its electron affinity using photoelectron spectroscopy, and compared the results with the fixed-dipole model described above, and with a recent calculation by Jordan [15].

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** Alfred P. Sloan Foundation Fellow.

2. Experimental arrangement

Most of the details of the experimental apparatus other than those for the ion source have been presented elsewhere [16]. The LiCl^- was produced in a low pressure, high temperature discharge ion source* which contained some LiCl (and KBr) crystals. The filament in the source was made from 15 mil W wire and run at ≈ 14 A of dc current. The resulting temperature of the source was estimated to be ≈ 1000 K. A discharge was then struck between the filament and an anode. The discharge was found to produce LiCl^- best when run at ≈ 40 V dc and ≈ 150 mA. A 40 mil hole in the anode allowed extraction of the ions with 1500 V applied between the anode and the first focusing electrode.

After the ions were decelerated to 680 eV, they were deflected 10° to remove neutrals from the beam. The ions were then mass selected with a Wien filter and directed into a field free interaction region, as shown in fig. 1. There the ions were crossed with a focused, intracavity beam of an argon-ion laser operating at 488 nm ($h\nu = 2.540$ eV). The energy of the photodetached electrons was determined by a hemispherical energy analyzer which had a resolution of ≈ 50 meV (fwhm) and the resulting spectrum was accumulated in a multichannel analyzer.

* Colutron Corporation, Boulder, Colorado 80302, USA.

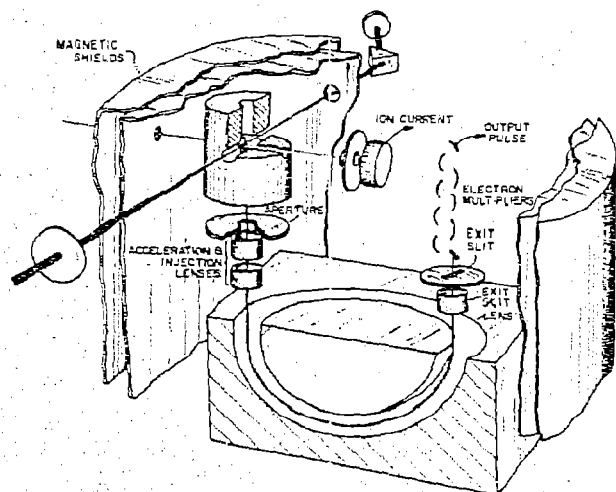


Fig. 1. Diagram of the interaction region. The LiCl^- ions were crossed with an Ar^+ laser ($h\nu = 2.540$ eV) and the energy of the resulting photodetached electrons analyzed by the hemispherical energy analyzer.

3. Results

With the source operated as described in section 2, LiCl^- beam currents of 0.5 nA were obtained in the interaction region. The identification of LiCl^- was confirmed by mass scans which showed a peak at mass 42 and another at mass 44 in the natural isotopic ratio of approximately 3:1 for Cl (mass 35) and Cl (mass 37).

The resulting photoelectron energy spectrum is shown in fig. 2. A scan of photodetached electrons for K^- was also taken, to determine the energy scale and eliminate any contact potentials. The peaks correspond to (v', v'') transitions from the v'' vibrational level of the ground electronic state of LiCl^- to the v' vibrational level of the ground electronic state of LiCl . The spacing of the three peaks is 88 ± 10 meV, in reasonable agreement with the 80 meV vibrational spacing of LiCl [17]. Other data also show a weak peak at 2.0 eV which could be the (0,1) transition due to thermal excitation in the source. Its location leads to a value of 60 ± 10 meV for the ω_e of LiCl^- .

Effects of the rotational distributions upon the positions of the peaks for LiCl^- shown in fig. 2 have been considered and indicate that any shifts will be much smaller than our present measuring errors.

The peaks at 1.94 eV, 1.85 eV and 1.76 eV are ascribed to the (0,0), (1,0) and (2,0) transitions respectively. If the peak at 1.94 eV were a transition with $v' > 0$, there would then be an observable peak appear-

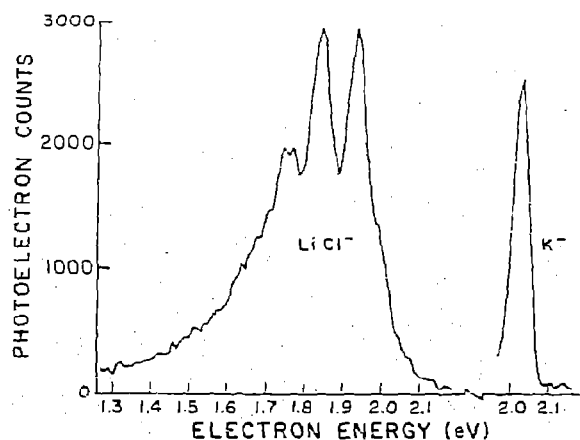


Fig. 2. Photoelectron energy spectrum of LiCl^- . The peaks at 1.94 eV, 1.85 eV, and 1.76 eV correspond to the (0,0), (1,0) and (2,0) transitions. A scan of K^- was used to calibrate the electron energy scale.

ing 80 mV higher in energy, due to the fact that Franck-Condon factors vary relatively slowly with ν' for transitions that originate from $\nu'' = 0$. Since the only other peak is one that is very weak and also located at 60 mV higher instead of 80 mV, we conclude that the peak at 1.94 eV is the (0,0) transition.

The ratios of the intensities of the (0,0), (1,0) and (2,0) transitions were used to calculate [16] the bond length of LiCl^- . Using simple harmonic oscillator wavefunctions, the Franck-Condon factors were studied as a function of the bond length difference between the ion and neutral. The resulting equilibrium distance for LiCl^- is

$$r_e = (4.12 \pm 0.08)a_0,$$

where the error arises from the uncertainty in the ω_e of LiCl^- and the nonlinearity of the transmission of the energy analyzer.

Using the value of 1.94 eV for the location of the (0,0) transition, we can determine the electron affinity of LiCl . Applying conservation of energy and momentum one obtains the following expression involving the electron affinity EA [16]

$$h\nu = \text{EA} + \Omega + mW/M + E_{\text{cp}}, \quad (1)$$

where $h\nu$ is the incident photon energy ($h\nu = 2.540$ eV), Ω is the laboratory energy of the detached photoelectron leaving the molecule in the ground vibrational level of the neutral molecule, m/M is the ratio of electron to ion mass, W is the kinetic energy of the ion, and E_{cp} is the contact potential energy difference between the interaction region and the electron energy analyzer. The mW/M correction is due to the transformation from center-of-mass frame to the laboratory frame. The E_{cp} is eliminated by simultaneously observing electrons from another ion whose EA is known. In this experiment we used K^- whose EA is (0.5012 ± 0.0005) eV [18].

Using eq. (1) for both LiCl and K , one eliminates E_{cp} and obtains:

$$\begin{aligned} \text{EA}(\text{LiCl}) = \text{EA}(\text{K}) + [\Omega(\text{K}) - \Omega(\text{LiCl})] \\ + mW\{1/M(\text{K}) - 1/M(\text{LiCl})\}. \end{aligned} \quad (2)$$

Therefore using the data shown in fig. 2 and applying eq. (2) we can obtain

$$\text{EA}(\text{LiCl}) = (0.61 \pm 0.02) \text{ eV}. \quad (3)$$

4. Comparison with theory

A number of researchers have studied a fixed dipole model which considers two point charges ($+e$ and $-e$) separated by a distance R , thus forming a dipole moment of magnitude eR . When $eR > 0.639 ea_0$, this dipole moment is capable of binding an extra electron. Wallis et al. [2] calculated the binding energy of such a system for various values of eR .

The dipole moment of LiCl is $2.79 ea_0$ [19]. Using this value, the theory of Wallis et al. [2] predicts that an electron in the ground state of LiCl^- should be bound by 4.68 eV, and that the first excited level should be bound 0.085 eV. It is very unlikely that the observed electrons have come from an excited state of LiCl^- . The reason that the experimental value of 0.61 eV is so much smaller than the theoretical value of 4.68 eV is undoubtedly due to the fact that the theory considers only a pure dipole field. This model is only appropriate at large distances, since it ignores the effects of core repulsion and the finite size of the atoms which are important at small distances.

Using the fixed dipole model, Turner et al. [20] have calculated the mean distance $\langle r_1 \rangle$ of the bound electron from the positive dipole charge. For a dipole moment of $2.79 ea_0$, they find that the mean distance $\langle r_1 \rangle$ is $1.79a_0$. Thus for the electrons bound by LiCl , the fixed dipole model predicts that the electron will be $\approx 1.79a_0$ from the Li^+ ion. Since this is comparable to the radius of the Li^+ ion ($\approx 1.29a_0$ [21,22]), overlap will occur and the effect of core repulsion will certainly be important.

Recently Jordan [15] has calculated the potential curve for LiCl^- . He finds that the electron affinity for LiCl is ≈ 0.5 eV, which is reasonably close to our experimental result. This difference is attributed [15] to correlation effects which have not as yet been included in the theory.

5. Conclusion

We have presented direct experimental evidence for the binding of an electron by the dipole moment of a neutral molecule. The binding energy of the electron in the LiCl^- ion is an order of magnitude smaller than the prediction of the fixed dipole theoretical model. More sophisticated theoretical models, such as the one being

developed by Jordan [15], which take account of the properties of a real molecule, are needed before accurate predictions can be made about the interaction of electrons in polar gases or other situations in which the effect of the dipole field is important.

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