

ELECTRON AFFINITY OF MgCl

Thomas M. MILLER¹ and W.C. LINEBERGER

*Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards,
and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA*

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The electron affinity of MgCl has been measured to be 1.589 ± 0.011 eV using photoelectron spectroscopy of an MgCl⁻ ion beam. Spectroscopic constants for (X¹Σ⁺)MgCl⁻ were found to be $\omega_e = 315 \pm 25$ cm⁻¹, $r_e = 2.37 \pm 0.01$ Å, $B_e = 0.211 \pm 0.002$ cm⁻¹, and $D_0(\text{Mg-Cl}^-) = 1.27 \pm 0.10$ eV. Preliminary results for MgI⁻ are also reported.

1. Introduction

We report here the first direct measurement of the electron affinity for an alkaline-earth monohalide, specifically, MgCl, as well as results on spectroscopic constants for MgCl⁻. This work is part of a program to study electrons bound by molecules with large dipole moments [1-5]. Törring et al. [6] have calculated 4.25 D for the dipole moment of MgCl. The present experiment was motivated by the quantitative and qualitative understanding that has been developed for bonding in the alkali halide negative ions [1]. The alkali halide results led us to expect that the electron affinities of the alkaline-earth monohalides would be in the neighborhood of 2 eV, an energy range which is convenient for possible threshold photodetachment studies of dipole-bound excited states.

2. Experimental

The experimental technique employed was laser photoelectron spectroscopy [7] of mass-selected MgCl⁻ ions. The method used to produce metal halide negative ion beams with a flowing afterglow ion source has been described earlier [1]. For the present experiments we followed the prescription of Ernst

and Kindt [8], evaporating a Mg/MgCl₂ mixture into the afterglow. The resulting mass-selected MgCl⁻ beam intensity (5×10^{-14} A) was far weaker than we had experienced with alkali halides [1], probably due both to the need to reduce MgCl₂ and to differences in the electron attachment processes. Electrons were photodetached with 100 W of intracavity radiation from an ArII laser operated at 488 nm (2.540 eV photons). Photoelectrons emitted perpendicular to both the ion and laser beams were energy analyzed with a hemispherical energy analyzer with resolution 10 meV full width at half maximum. The electron energy scale was calibrated by photodetaching O⁻ [9] and W⁻ [10,11].

3. Results

The photoelectron energy spectrum for MgCl⁻ is shown in fig. 1. The vibrationless transition MgCl(*v'*=0) ← MgCl⁻(*v''*=0) is readily identified in the spectrum because the peak spacing to the left corresponds to the known [12] vibrational spacing in neutral MgCl. The electron binding energy in MgCl⁻ (the electron affinity of MgCl) is the difference between the 2.540 eV photon energy and the measured electron kinetic energy corresponding to the (0-0) origin peak. A 3 meV correction is made for the shift of the peak of the origin band due to unresolved rotational transitions, as detailed in ref. [1].

¹ Permanent address: Department of Physics and Astronomy, University of Oklahoma, Norman, OK 73019, USA.

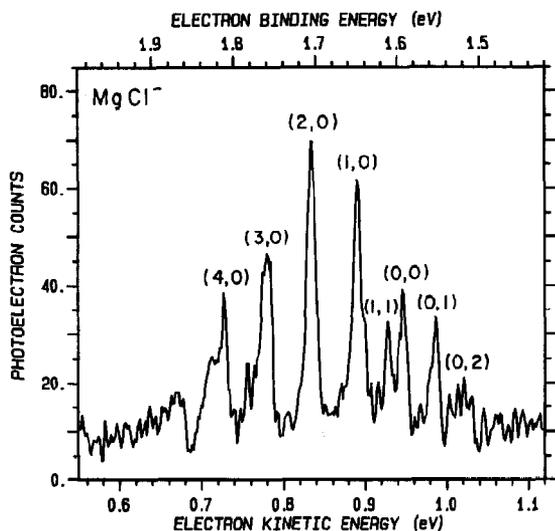


Fig. 1. Photoelectron kinetic energy spectrum for MgCl^- at 488 nm. The numbers in parentheses give the final (neutral molecule) and initial (negative ion) vibrational quantum numbers, respectively.

The peak spacing to the right of the origin band gives the vibrational frequency ω_e'' in the negative ion. A more precise value for ω_e'' for MgCl^- is determined by an anharmonic Franck-Condon fit to the data in which all of the "hot band" structure is modeled as described in ref. [1]. The Franck-Condon fit also yields the change in the equilibrium internuclear separation, $|r_e'' - r_e'|$, between the negative ion and the neutral molecule. We assume that $r_e'' > r_e'$ since our measured force constant and bond energy for the negative ion are less than those for the neutral molecule. The anharmonicity parameter $\omega_e x_e''$ is too small ($< 20 \text{ cm}^{-1}$) to be determined from these data. The results are summarized in table 1. B_e'' and r_e'' for

Table 1

Spectroscopic constants for MgCl^- . The first three quantities were determined directly from the data. The final three numbers were derived from the measured quantities and known (ref. [12]) spectroscopic quantities for the neutral molecule

Quantity	Value
electron binding energy	$1.589 \pm 0.011 \text{ eV}$
ω_e''	$315 \pm 25 \text{ cm}^{-1}$
$r_e'' - r_e'$	$0.17 \pm 0.01 \text{ \AA}$
r_e''	$2.37 \pm 0.01 \text{ \AA}$
B_e''	$0.211 \pm 0.002 \text{ cm}^{-1}$
$D_0(\text{Mg-Cl}^-)$	$1.27 \pm 0.10 \text{ eV}$

$(X^1\Sigma^+)\text{MgCl}^-$ were derived from our results using the known [12] B_e' and r_e' for $(X^2\Sigma^+)\text{MgCl}$. The 0.011 eV uncertainty in $EA(\text{MgCl})$ contains contributions of $\pm 3 \text{ meV}$ related to energy scale calibration and $\pm 3 \text{ meV}$ due to the rotational correction; the remainder of the quoted uncertainty is statistical. The uncertainties in ω_e'' and r_e'' reflect the quality of the Franck-Condon simulation of the data. The anion dissociation energy, $D_0(\text{Mg-Cl}^-)$, was deduced using the thermochemical cycle,

$$D_0(\text{Mg-Cl}^-) = D_0(\text{Mg-Cl}) + EA(\text{MgCl}) - EA(\text{Cl}) \quad (1)$$

$D_0(\text{Mg-Cl})$ was obtained from ref. [12] and the electron affinity (EA) of Cl from ref. [13].

4. Discussion

The electron affinity measured here for MgCl can be qualitatively understood on the basis of the model developed for the alkali halides by Jordan and Luken [14], namely, that of a halide negative ion near to and strongly polarizing a neutral alkali (or Mg) atom, greatly weakening the bond energy of a valence electron. By analogy with the alkali halide case [1], it is a valence electron of the Mg atom that is photodetached. The electron binding energy in MgCl^- should be greater than in its neighbor NaCl^- .

This correspondence can be somewhat quantified. In ref. [1], an electrostatic model [6] was applied to obtain electron affinities for the alkali halides accurate to within about 0.1 eV. MgCl and MgCl^- should fit this model, since the calcium monohalides are considered to be completely ionic bonded [15-18]. We used the equations of ref. [1] and [6], properly accounting for the two valence electrons outside of a Mg^{2+} kernel, in the case of MgCl^- . "Free ion" polarizabilities were employed, as described by Törring et al. [6]. The results are not as good as in the simpler case of the alkali halides. The model [6] does not consistently estimate the molecular bond energies of the neutrals and negative ions. For the alkali halides [1], both the anion and the neutral bond strengths given by the model were low, but the errors tended to cancel in calculating electron affinities from the energy balance analogous to that of eq.

(1). In the application to the MgCl system, the calculated negative ion bond energy $D_0(\text{Mg}-\text{Cl}^-)$ is within 1% of the experimental value (table 1), but the calculated bond energy for the neutral is 26% low, making the predicted electron affinity high by 44%. Still, the electrostatic model is correct in predicting higher electron affinities for the alkaline earth monohalides than for the alkali halides (≈ 2 eV versus ≈ 0.7 eV). More sophisticated approaches (the ligand field method of Bernath et al. [15] and Rice et al. [16] and the electrostatic model of Kleinschmidt and Hildenbrand [18]) may be preferable if applied consistently to MgCl and MgCl^- .

Preliminary data have been obtained for MgI^- with a much weaker intensity (10^{-14} A). An electron affinity for MgI of 1.90 ± 0.04 eV is observed, and $\omega_e'' = 190 \pm 45$ cm^{-1} for $(X^1\Sigma^+)\text{MgI}^-$. Using the MgI bond dissociation energy (ref. [18], 1.95 ± 0.22 eV) and EA(I) from ref. [19], the anion dissociation energy, $D_0(\text{Mg}-\text{I}^-) = 0.79 \pm 0.26$ eV, follows from the thermochemical cycle analogous to eq. (1).

5. Summary

We have used photoelectron spectrometry of MgCl^- to determine the electron affinity of MgCl, 1.589 ± 0.011 eV, and a bond length and vibrational frequency for $(X^1\Sigma^+)\text{MgCl}^-$ (table 1). Similar results are reported for MgI.

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