HIGH-RESOLUTION PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF Cl_2: THE GROUND ($X^+\ ^2\Pi_g$) AND FIRST EXCITED ($A^+\ ^2\Pi_u$) ELECTRONIC STATES OF Cl_2^+

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Recently, two studies have been devoted to the low-lying electronic states of Cl_2^+, one by PFI-ZEKE photoelectron (PE) spectroscopy of the $X^+ \leftarrow X$ transition[a] and one by laser-induced-fluorescence spectroscopy of the $A^+ \rightarrow X^+$ band system[b]. To complement the information available on the X^+ and A^+ electronic states of Cl_2^+, we have recorded partially rotationally resolved single-photon PFI-ZEKE PE spectra of the $X^+\ ^2\Pi_{g,i} \leftarrow X\ ^1\Sigma_g^+$ and $A^+\ ^2\Pi_{u,i} \leftarrow X\ ^1\Sigma_g^+$ ($i = 3/2,\ 1/2$) photoionizing transitions of Cl_2 in the wavenumber ranges $92\,500 - 96\,500\ \mathrm{cm}^{-1}$ and $106\,750 - 115\,500\ \mathrm{cm}^{-1}$. These regions correspond to transitions to low-lying vibrational levels of the X^+ state with $v^+ = 0 - 5$ and to transitions to vibrational levels of the X^+ state with $v^+ = 25 - 45$ and vibrational levels of the A^+ state with $v^+ \leq 7$.

The analysis of the rotational structure and the isotopic shifts of these spectra has enabled the derivation of an improved value of the first adiabatic ionization energy ($92\,647.7 \pm 0.3\ \mathrm{cm}^{-1}$ for $^{35}Cl_2$). In combination with measurements of ion-pair states with $n \approx 1800$[c], new values for the dissociation energies D_0 of Cl_2 and Cl_2^+ could also be derived. The potential energy function of the X^+ state of Cl_2^+ was determined in a least-squares fitting procedure. Spin-orbit splittings were derived for many vibrational levels of the X^+ and A^+ states. Combining our results with other results[b,d,e,f], several low-lying vibrational levels of the upper spin-orbit component of the A^+ state could be assigned for the first time. The PFI-ZEKE PE spectra also contain a series of as yet unassigned lines and reveal numerous perturbations.

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