

Renner-Teller Effect in $\text{HCCCl}^+ (\tilde{X}^2\Pi)$ Studied by High Resolution Photoelectron Spectroscopy

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Synopsis The spin-vibronic energy levels of $\text{HCCCl}^+ (\tilde{X}^2\Pi)$ up to 4000 cm^{-1} above the vibrational ground state have been measured. The spectroscopic parameters have been determined. By analyzing the partially resolved rotational spectrum, the first adiabatic ionization energy of HCCCl is determined as $85497.5 \pm 2.0 \text{ cm}^{-1}$ ($10.6003 \pm 0.0003 \text{ eV}$), improving the accuracy of the reported data by two orders.

The coupling of electronic motion and nuclear vibration in linear molecules (the Renner-Teller effect) serves as a typical example of the breakdown of the Born-Oppenheimer approximation. Although the Renner-Teller effect of triatomic molecules has been extensively studied both experimentally and theoretically, there have been few studies on linear tetra-atomic molecules. In contrast to triatomics, tetra-atomic molecule has two degenerate bending vibrations that are Renner-Teller (RT) active. The two mode RT coupling effect is meaningful but poorly understood to our knowledge.

The HCCCl^+ cation is an attractive candidate for studying the Renner-Teller effect of tetra-atomic molecules. However, few high resolution spectroscopic data are available now. In this work, using high resolution photoelectron spectroscopic (ZEKE) method in combining with a tunable coherent XUV radiation producing by four-wave mixing, the vibrationally resolved photoelectron spectrum of HCCCl is recorded, allowing a complete description of the angular momentum coupling effects and the determination of the Renner-Teller parameters ϵ_4 , ϵ_5 , and ϵ_{45} for the first time.

An effective Hamiltonian including two-mode Renner-Teller coupling parameters is employed to assign the spectrum [1]. The main results are demonstrated in Figure 1. The first column shows the energy levels calculated by harmonic-oscillator model. In the second and third columns the spin-orbit interaction and Renner-Teller effect are added successively. The calculated energy levels are in good

agreement with the experimental values (the last column).

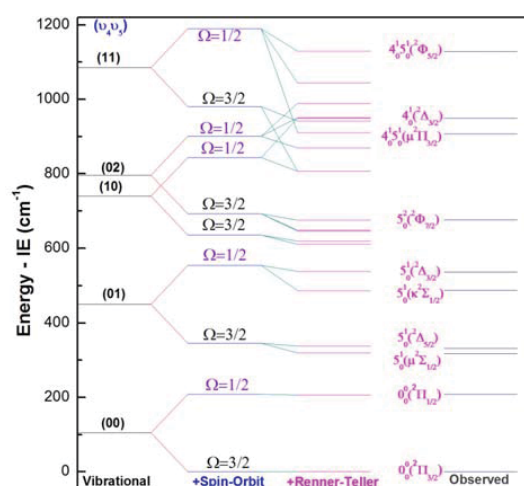


Figure 1. The calculated and observed low-lying vi-vibronic energy levels of $\text{HCCCl}^+ (\tilde{X}^2\Pi)$.

It is seen from the above diagram that the Renner-Teller effect in $\text{C}\equiv\text{C}-\text{H}$ bending mode ν_4 is apparent, while in $\text{C}\equiv\text{C}-\text{Cl}$ bending mode ν_5 is partially quenched by the spin-orbit interaction, because the spin-orbit interval is close to the fundamental frequency of mode 5. A strong coupling between the vibrational modes ν_4 and ν_5 is also found. The results found in this work provide new insights into the Renner-Teller effect in tetra-atomic molecules.

References

- [1] S He *et al* 2005 *J. Chem. Phys. Ser.* **123** 014316

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