

Infrared Spectra of $\text{CH}_3^+-\text{He}_2$

(Univ. Köln^a, Hiroshima Univ.^b, AIST^c)

Matthias Töpfer, Philipp C. Schmid, Hiroshi Kohguchi,
Koichi M. T. Yamada, Stephan Schlemmer, and Oskar Asvany

In the previous study we reported pure rotational spectra of the cluster ion CH_3^+-He (Me^+He) stored in a cryogenic ion-trap [1], where IR-MW double resonance spectroscopy was employed in combination with the IR photo-dissociation (IRPD) spectroscopy. As a natural extension, we have studied the weakly bound $\text{CH}_3^+-\text{He}_2$ complex (Me^+He_2), which is most likely a symmetric top of D_{3h} symmetry, i.e. $\text{He}-\text{CH}_3^+-\text{He}$. In contrast to CH_3^+-He (Me^+He) of C_{3v} symmetry, the complex has no permanent dipole moment, and therefore we could not apply pure rotational spectroscopy. Therefore, we have examined its ν_3 fundamental band (C–H deg. str.) by the conventional IRPD. Figure 1 shows the infrared spectrum of Me^+He_2 observed for the first time.

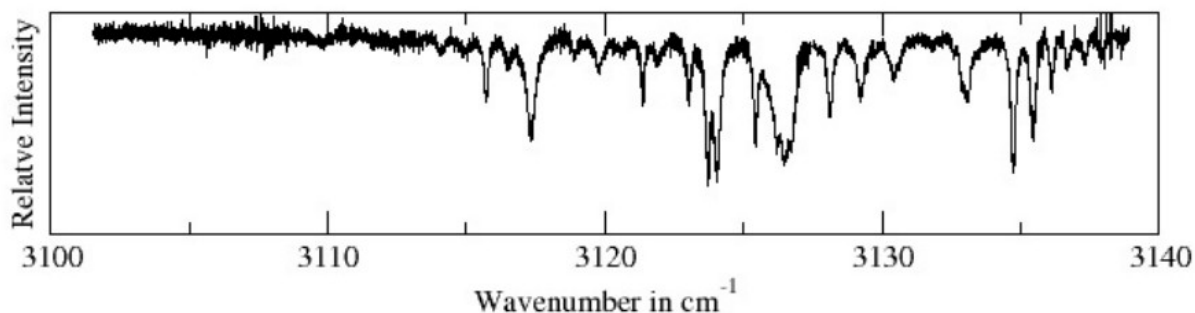


Fig. 1: Infrared spectrum of Me^+He_2 observed by IRPD in the 4K ion trap.

Me^+ ions are created in a storage ion source from methane (CH_4 , 99.9%) by electron impact ionization. By mass-filtering ($m = 15$ u) with a linear quadrupole a pulse of around 20000 ions is guided into the 22-pole ion trap of 22-pole mounted on a closed-cycle 4 K cooler. A few ms before the ion pulse reaches the trap, He buffer gas is injected into the trap housing via a piezo valve, in order to cool the ions by collisions with the buffer gas. During the trapping period (1.7 s) the trapped ions are irradiated by narrow-band cw infrared light, leading to excitation upon resonance and the destruction of the complex within a few ps. Then the ions are mass-filtered for Me^+He_2 ($m = 23$ u) by a second linear quadrupole and counted by a Daly-type detector. The IRPD spectrum is recorded by counting the number of Me^+He_2 complexes as a function of excitation frequency as shown; the resonant absorption of IR photons is seen as a dip in the Me^+He_2 counts.

Although there are a few investigations on Me^+ and Me^+He reported in the literature, both experimentally and computationally, e.g. Refs. [1–4], we could not find any for the

cluster ion Me^+He_2 . In Fig. 2 the vibrational term values so far known, or predicted, are illustrated for Me^+ , Me^+He and Me^+He_2 , where the $\nu_3=1$ term value of Me^+He_2 is that determined in the present work. Assignments and analysis of the spectra were carried out by the program tool, PGOPHER [5]. The serious anomaly found for the $K=1$ levels in the $\nu_3=1$ excited state will be discussed.

	CH_3^+		$\text{CH}_3^+\text{-He}$		$\text{CH}_3^+\text{-He}_2$
ν_3 E'	————— 3108.38	—————	3115.58	—————	3121.76
ν_1 A_1'	————— 2903	—————	2946.39	—————	
ν_4 E'	————— 1370	—————	1361	—————	
ν_2 A_1''	————— 1350	—————	1337	—————	
		ν_r A_1	————— 570	—————	A_1'
		ν_θ E	————— 193	—————	A_1''
				—————	E'
				—————	E''

Fig. 2: Vibrational energy levels of Me^+ , Me^+He and Me^+He_2 are illustrated. The experimental energy term values are given in the right side of the levels in roman, and those predicted by *ab initio* calculations are in italic. The modes ν_r and ν_θ represent the C–He stretching and bending vibration, respectively.

References

- [1] M. Töpfer, T. Salomon, S. Schlemmer, O. Dopfer, H. Kohguchi, K. Yamada, and O. Asvany, *Phys. Rev. Lett.* **121**, 143001 (2018).
- [2] R. V. Olkhov, S. A. Nizkorodov, and O. Dopfer, *J. Chem. Phys.* **110**, 9527 (1999).
- [3] M. W. Crofton, M. Jagod, B. D. Rehfuss, W. A. Kreiner, and T. Oka, *J. Chem. Phys.* **88**, 666 (1988).
- [4] D. J. DeFrees and A. D. Mlean, *J. Chem. Phys.* **82**, 333 (1985).
- [5] M. Western, “PGOPHER: A program for simulating rotational, vibrational and electronic spectra,” *J. Quant. Spectrosc. Radiat. Transfer*, **186**, 221 (2017).