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Note: Photoelectron spectroscopy of cold UF_5^-

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Recently, we reported the photoelectron spectra of UF_5^- at room temperature (RT) in combination with relativistic quantum calculations.¹ Both UF_5^- and UF_5 were known to have C_{4v} symmetry, derived from the removal of one F atom from the octahedral UF_6 . But there is a large U-F bond length change between the ground states of the anion and neutral UF_5 , resulting in a long vibrational progression in the photoelectron spectra. In principle, the photoelectron spectra should yield accurately the electron affinity (EA) of UF_5 from the 0-0 vibrational transition in the ground state photodetachment band. However, because of the presence of vibrational hot bands, the 0-0 transition was not clearly resolved in the RT photoelectron spectra in the recent study. Instead, the EA of UF_5 was evaluated using a Franck-Condon analysis as 3.82 ± 0.05 eV. The Franck-Condon analysis also yielded a vibrational frequency of 650 ± 50 cm^{-1} for the totally symmetric U-F stretching mode in UF_5 and a vibrational temperature of ~ 350 K for the UF_5^- anion. In the meantime, we have built a cryogenically cooled ion trap,² which allows photoelectron spectra of cold anions to be obtained. In this Note, we report the photoelectron spectra of vibrationally cold UF_5^- . From the clearly resolved 0-0 transition, we are able to measure the EA of UF_5 more accurately as 3.885 ± 0.015 eV.

We first demonstrated vibrational cooling in a cryogenically cooled Paul trap in photoelectron spectroscopy of multiply charged anions.³ The vibrational cooling was shown by the observations of temperature-dependent conformation changes,^{4,5} H_2 van der Waals complexes,⁶ and the elimination of vibrational hot bands in a very large molecule containing 121 atoms in $\text{C}_{120}\text{O}^{2-}$.⁷ The H_2 -tagging using the cryogenically cooled Paul trap has since been successfully employed for infrared vibrational spectroscopy of cold ions.⁸ The current cold ion trap is an improved version of the originally designed cryogenically cooled Paul trap³ by pulsing the thermalization gas,⁸ instead of continuous flow. Details of the new trap will be published in Ref. 2. The electrospray conditions to produce the UF_5^- anions were identical to the previous room temperature study.¹

Figures 1(a)–1(c) display the photoelectron spectra of UF_5^- at three different detachment photon energies with the ion trap operated at 4.4 K, compared to the corresponding RT spectra (Figs. 1(d)–1(f)). Even though the magnetic-bottle photoelectron analyzer is the same as the RT study, the low temperature spectra are substantially improved due to the elimination of vibrational hot bands. In addition to the better resolved vibrational structures in the low temperature

spectra, we also observed that the two vibrational peaks near the threshold (high binding energy side) in the 275 and 266 nm spectra were enhanced. These were observed as a tail in the RT spectra (not shown previously¹) and were thought to be possible artifacts in the magnetic-bottle detector for low energy electrons. The low temperature data with the clear vibrational resolution suggest that the enhancement is real and could be due to a near threshold resonant effect. However, we have never observed such a near threshold enhancement before. In fact, our magnetic-bottle analyzer tends to disfavor the detection efficiency of low energy electrons. The 245 nm spectrum has relatively low electron count rates and poor signal to noise ratios, in particular, in the high binding energy side above ~ 4.7 eV relative to the RT spectrum.

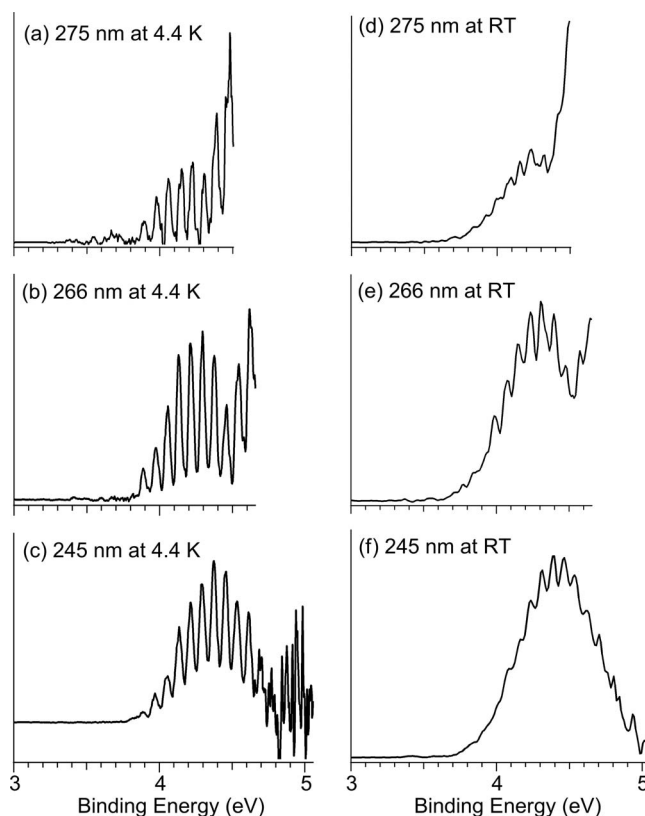


FIG. 1. Photoelectron spectra of UF_5^- at an ion trap temperature of 4.4 K (left), compared to those taken at room temperature (right)¹ at (a) and (d) 275 nm (4.508 eV), (b) and (e) 266 nm (4.661 eV), and (c) and (f) 245 nm (5.061 eV).

The first vibrational peak at 3.885 eV in the low temperature data defines the adiabatic or 0-0 transition and the EA of neutral UF₅. In general, one cannot guarantee the first peak to be the 0-0 transition with such a long Franck-Condon profile. However, we are confident about this assignment on the basis of the Franck-Condon simulations and theoretical calculations reported in our recent RT study.¹ Taking into account of the accuracy of the calibration, we report the EA of UF₅ as 3.885 ± 0.015 eV, which is significantly improved relative to the value obtained in our recent RT study or the estimate of 4 ± 0.4 eV using charge transfer.⁹ The U-F vibrational frequency obtained from the low temperature data is the same as before.¹

In conclusion, we have measured photoelectron spectra of vibrationally cold UF₅⁻ and obtained a more accurate EA for UF₅ as 3.885 ± 0.015 eV.

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