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The vacuum UV photoabsorption spectroscopy of vinyl fluoride (C_2H_3F): The vibrational fine structure and its analysis

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ABSTRACT

The vacuum UV photoabsorption spectrum of C_2H_3F has been examined in detail between 6 eV and 25 eV photon energy by using synchrotron radiation. The analysis of the data is supported by ab initio quantum mechanical calculations applied to valence and Rydberg excited states of C_2H_3F. At 7.6 eV the $\pi \rightarrow \pi^*$ and the $2a'' \rightarrow 3s$ transitions are observed. An analysis is proposed and applied to the mixed fine structure belonging to these transitions. For the $\pi \rightarrow \pi^*$ transition one single long vibrational progression is observed with $hc\omega_e = 95 \pm 7$ meV (766 ± 56 cm^{-1}) and its adiabatic excitation energy is 6.892 eV (55 588 cm^{-1}). The $2a'' \rightarrow 3s$ transition is characterized by a single short progression with $hc\omega_e = 167 \pm 10$ meV (1350 ± 80 cm^{-1}) starting at 6.974 eV (56 249 cm^{-1}). From the present ab initio calculations these two wavenumbers best correspond to the vibrational modes υ_9 (CH_2 rock in-plane, FCC-bend) and υ_6 (CH_2 rock in-plane, CF stretch) calculated at 615 cm^{-1} in the π^* state and 1315 cm^{-1} in the $(^2A'')$3s Rydberg state respectively. The C=C stretching could not be excluded. The dense structured spectrum observed between 8.0 eV and 10.5 eV has been analyzed in terms of vibronic transitions to Rydberg states all converging to the $C_2H_3F^+(\tilde{X}A'')$ ionic ground state. An analysis of the associated complex fine structure of the individual Rydberg states has been attempted providing average values of the wavenumbers, e.g., for the $(^2A'')$3p Rydberg state $hc\omega_9 = 60 \pm 1$ meV (or 484 ± 8 cm^{-1}), $hc\omega_7 = 151 \pm 7$ meV (or 1218 ± 60 cm^{-1}), $hc\omega_4 = 191 \pm 3$ meV (or 1540 ± 24 cm^{-1}). The assignment of $hc\omega = 105 \pm 5$ meV (or 823 ± 40 cm^{-1}) is discussed. These experimental values are in good agreement with the theoretical predictions for $C_2H_3F^+$ [R. Locht, B. Leyh, D. Dehareng, K. Hottmann, H. Baumgärtel, Chem. Phys. (in press)]. Above 10.5 eV and up to 25 eV several broad and strong bands are tentatively assigned to transitions to valence (V–V) and/or Rydberg (V–R) states converging to excited ionic states of C_2H_3F.

1. Introduction

In previous investigations the combined use of vacuum UV photoabsorption (VUV-PAS), He(I) (PES), threshold (TPES), constant ion state (CIS) photoelectron spectroscopies, photoionization mass spectrometry (PIMS) and photoion translational energy spectroscopy allowed us to get a deeper insight into the various aspects of the dissociation dynamics of molecular ions. Parallel to these experimental techniques ab initio quantum mechanical calculations were applied. In the recent past, we thoroughly investigated several molecular systems, e.g. the monohalogenated derivatives of methane CH_3F [1–5], CH_3Cl [6–8] and CH_3Br [9–11].

The energy and structure of the neutral as well as the ionic ground and excited states of ethylene and its halogenated derivatives are of considerable interest for understanding the photochemistry of this extremely important class of compounds involved in many fields of chemistry. Furthermore, another and more fundamental motivation of this work is the systematic investigation of the influence of the position and nature of the substituent on the dynamics of the molecular ions. The systematic study of ethylene and of several of its halogen substituted derivatives has been initiated, e.g. for C_2H_3Cl [12,13], C_2H_3Br [14–16] and 1,1-$C_2H_2F_2$ [17,18], or is in progress using the same array of techniques.

The vacuum UV spectroscopic data reported on vinyl fluoride are very scarce. To the best of our knowledge the latest detailed work devoted to this molecule has been reported by Bélanger and Sandorfy [19]. These authors analyzed the vacuum UV spectrum of the six fluoroethylenes in the 50 000–82 000 cm^{-1} (6.2–10.2 eV) spectral region using a 1 m normal incidence (1 m-NIM) monochromator equipped with a 1200 l/mm grating. The observed features were classified and assigned to valence → valence ($\pi \rightarrow \pi^*$) and valence → Rydberg transitions. A vibrational analysis of the $2a'' \rightarrow 3p$ Rydberg transition was also presented.

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The valence–shell electron energy-loss spectroscopy (VSEELS) technique is closely related to vacuum UV photoabsorption spectroscopy. Sze et al. [20] reported the results obtained for the monohalogenated ethylenes between 6 and 22 eV electron energy-loss and with about 35 meV energy resolution. Rydberg series and their vibrational analysis have been reported.

Recently, ab initio quantum mechanical calculations have been carried out on C_2H_3F to investigate the excited state energy surfaces [21]. The vertical spectrum at planar geometry including 3s and 3p Rydberg states has been calculated. The existence of several conical intersections has been demonstrated for different geometries.

The aim of this paper is to report the vacuum UV photoabsorption spectrum of vinyl fluoride (i) for the first time in the 10–25 eV photon energy range at low resolution and (ii) in the 6–11 eV spectral region at high resolution. The fine structure observed in this latter region will be analyzed in detail, with the help of high level quantum chemistry calculations.

2. Experimental

2.1. Experimental setup

The experimental setup used in this work has already been described in detail elsewhere [15]. Only the most salient features will be reported here. Furthermore, two monochromators were available at the BESSY synchrotron radiation facilities.

Synchrotron radiation available from the BESSY I facility (Berlin, Germany) was dispersed with a modified vacuum UV normal incidence 225 McPherson monochromator with a focal length of 1.5 m, instead of 1 m in the commercial version (1 m-NIM-2 beamline). A laminar Zeiss grating is used for the efficient reduction of the 2nd spectral order. It is gold coated with 1200 l/mm and its transmission breaks down above 26 eV (210 000 cm^{-1} or 48 nm). The width of the entrance and exit slits of 100 μm ensures a 0.1 nm wavelength resolution corresponding to a resolving power of about 1200 at 10 eV. This monochromator has been used for the recording of low-resolution absolute photoabsorption spectra in the 5–25 eV photon energy range.

The 3 m-NIM-2 beamline at the BESSY II facility (Berlin, Germany) has been described by Reichardt et al. [22]. This 3 m-NIM monochromator is positioned at a bending magnet frontend. It is equipped with two spherical gratings, i.e., an Al/MgF_2-grating of 600 l/mm and a Pt-grating of 2400 l/mm allowing to cover the 5–55 eV photon energy range. The latter grating has its optimal transmission between 10 and 40 eV (124–31 nm). The entrance and exit slits were adjusted between 10 and 40 μm leading to a resolving power of about 25 000 to 13 000 at 10 eV (124 nm) photon energy. This monochromator was used for recording high resolution spectra. Most of the spectra discussed in the present work were measured with 40 μm entrance and 10 μm exit slits and using the 600 l/mm Al/MgF_2-grating.

In all above described setups, the light has to pass, at the exit slit of the monochromator, through a 1 mm thick stainless steel microchannel plate necessary to maintain a differential pressure of 1:1000 before entering a 30 cm long stainless steel absorption cell. Most spectra are recorded without filter on the light path. However, in some cases, a LiF filter (cutoff at 11.8 eV or 95 000 cm^{-1} or 105 nm) is used, which can be inserted in the light beam without vacuum breakdown. The vapor pressure in the cell is measured by a Balzers capacitor manometer. The light is detected by a sodium salicylate sensitized photomultiplier located at the end of the absorption cell and in front of the absorption cell entrance slit. Output pulses are recorded by a 100 MHz counter. The recording of an absorption spectrum requires one scan with gas in the absorption cell and one with the evacuated cell. The stability of the synchrotron radiation and of the pressure in the cell ensured reliable absorption data. If necessary, the spectra presented in the following sections are corrected for any pressure drift. The sample pressure has been maintained at 25–30 μbar to avoid saturation. The commercially available C_2H_3F, purchased from Fluochem Ltd and of 99.5% purity, was used without further purification.

2.2. Data handling and error estimation

As will be mentioned in the next sections, weak sharp peaks and diffuse structures are often superimposed on a strong continuum. To make the characterization of these features easier a continuum subtraction procedure has been applied. This method has already been used successfully in previous spectral analyses [5,23]. For this purpose, the experimental curve is severely smoothed to simulate the underlying continuum which is then subtracted from the original photoabsorption spectrum. The smoothing procedure consists in filtering the experimental curve by fast Fourier transform (FFT). The weak features emerge from a remaining strongly attenuated background. The resulting diagram will be called Δ-plot in the forthcoming sections.

The wavelength calibration of the 1.5 m-NIM monochromator has been performed by using the Ar^+ absorption spectrum between the $^2P_{3/2}$ and the $^2P_{1/2}$ ionic states. The accuracy of this calibration is better than 2 meV. In the measurements between 10 eV and 25 eV photon energy, the photoabsorption spectrum has been recorded with an energy interval of about 4 meV. The error on the energy position of a feature is estimated to be 6 meV. In the photoabsorption spectra between 6 eV and 11 eV, an energy increment of 1 meV has been adopted. The error on the energy position of a feature is estimated to be of the order of 2 meV. This evaluation is confirmed by the reproducibility of energy positions measured in different spectra recorded over several years.

3. Experimental results

The good control of the experimental parameters allows us to display the spectra in terms of the molecular extinction coefficient $\varepsilon_{h\nu}$ as a function of the photon energy (eV).

(i) Fig. 1a displays the low-resolution PAS measured with 4 meV increments between 10 eV and 25 eV photon energy. Above 22 eV the transmission of the grating rapidly decreases resulting in a rapid degradation of the signal-to-noise ratio. Fig. 1b shows the Δ-plot used to enhance the weak structures present in the original spectrum. It is obtained by the subtraction procedure described in Section 2.2.

The most salient features are marked by vertical bars and their position in energy are listed in Table 1.

It has to be emphasized that the high-energy features observed between 10 eV and 20 eV in this PAS are by far stronger than in the PAS of C_2H_3Br [14]. Fig. 1b shows that several bands are superimposed by a fine structure, e.g. in the 10.476–14.185 eV energy range.

(ii) Fig. 2a displays the high-resolution photoabsorption spectrum as observed between 6.0 eV and 10.5 eV and recorded with 1 meV photon energy increments. Fig. 2b shows the Δ-plot obtained by the subtraction procedure. Numerous sharp structures are thus obtained superimposed on a strongly weakened background. The vibrationless transitions corresponding to the Rydberg excitations are marked by vertical bars. The energy positions of the Rydberg transitions are listed in Table 2 together with their quantum defects and convergence limits.