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Characterisation of a new VUV beamline at the Daresbury SRS using a dispersed fluorescence apparatus incorporating CCD detection

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Abstract: The design and performance of a new normal incidence monochromator at the Daresbury Synchrotron Radiation Source, optimised for experiments requiring high flux of vacuum-UV radiation, are described. The re-developed beamline 3.1, based on the Wadsworth design of monochromator, is the source of tunable vacuum-UV photons in the range 4 – 31 eV, providing over two orders of magnitude more flux than the vacuum-UV, Seya monochromator in its previous manifestation. The undispersed and dispersed fluorescence spectra resulting from photoexcitation of N₂, CO₂, CF₄ and C₆F₆ are presented. Emitting species observed were N₂⁺ \( B²Σ_u^+ ← X²Σ_g^+ \), CO₂⁺ \( A²Π_u ← X²Π_g \) and \( B²Σ_u^+ ← X²Π_g \), CF₄⁺ \( C²T₂ ← X²T₁ \) and \( C²T₂ ← A²T₂ \), CF₃⁺ \( A²Σ_u ← A²Σ_u \) and \( C₆F₆⁺ \( B²Σ_u ← X²E_{1g} \). A CCD multi-channel detector has significantly reduced the time period needed to record dispersed fluorescence spectra with a comparable signal-to-noise ratio.

1. Introduction

Beamline 3.1 of the Daresbury Synchrotron Radiation Source (SRS) has recently been re-developed in order to provide \( ca. \) two orders of magnitude higher flux than it had in its previous manifestation. This improvement has been achieved by a design that comprises a minimal number of optical components, thus substantially reducing the effect of transmission losses. The chosen monochromator has the Wadsworth configuration, which contains only a concave diffraction grating [1], and is a great simplification over the previously-installed Seya monochromator, where concave mirrors were positioned both before and after the entrance and exit slits. A further feature of this new SRS monochromator is that
it has no entrance slit, so it makes efficient use of the available horizontal aperture of the synchrotron radiation beamline. In this paper we report initial results using a dispersed fluorescence apparatus to aid the commissioning of this new facility. Such experiments in the gas phase have never routinely been performed on any VUV beamline at the Daresbury SRS due to insufficient flux from the current suite of monochromators. These experiments were chosen for their comparative simplicity, previous success having been obtained using a similar apparatus at the BESSY1 synchrotron in Berlin [2]. The main enhancement of our current equipment over that used in Berlin is the use of a charge-coupled device (CCD) detection system. This multi-channel detector permits the measurement of a wide range of wavelengths simultaneously, as opposed to the photomultiplier tubes used at BESSY1, where a grating must scan over a defined spectral range and successive wavelengths are focussed through an exit slit onto the photomultiplier tube. In essence, the CCD can attain the same signal/noise ratio as that achieved by single-channel detector in a much shorter acquisition time, \textit{i.e.} the Jacquinot advantage [3]. The samples we have studied are N$_2$, CO$_2$, CF$_4$ and C$_6$F$_6$. They were chosen both for their well-established spectroscopy and for their non-corrosive nature, thereby implying ease of handling.

2. Experimental

2.1 The new Wadsworth monochromator

The monochromator is based on the Wadsworth principle [1], and is similar in layout to that built for the DESY synchrotron over three decades ago [4]. The advantage in using this type of monochromator on a bending magnet of a synchrotron radiation source is that it has a large aperture, and by using the source as its entrance slit makes optimum use of the radiation available. This instrument operates in horizontal dispersion, so its resolution is limited by the horizontal electron beam size in the storage ring, FWHM \textit{ca.} 1.8 mm in the case of the SRS, corresponding to a best resolution of \textit{ca.} 0.05 nm. Although this is a factor of five inferior to that which could be obtained using vertical dispersion, it is sufficient for the kinds of experiment envisaged for this beamline, and led to a much more convenient experimental arrangement. The scanning mechanism is by means of an off-axis pivot [5,6], which makes an approximate correction for the changing focus of the grating for different wavelengths. The main difference with this monochromator over previous instruments of this kind is that the length of the pivot arm can be varied externally to the vacuum. This means that different wavelength ranges can be covered without substantial loss in resolution; the user chooses the wavelength region required and adjusts the pivot arm to give optimum performance in that region. The position of the exit slit, \textit{i.e.} the grating to exit slit distance, GS (see Figure 1), can also be changed externally, allowing further optimisation of the wavelength resolution over a given spectral range. Three gratings can be mounted, though only two have been fitted at the time of writing, interchangeable under vacuum, giving a wide range of wavelength coverage, currently \textit{ca.} 40 – 200 nm. The high-energy grating, 2400 lines/mm, covers best the range 40 – 100 nm; the medium-energy grating, 1200 lines/mm, covers best the range 80 – 200 nm.
The optical layout, seen in plan view from above, is shown in Figure 1. The monochromator is preceded by a water-cooled metal plane mirror, which deflects the incident radiation through 20° onto the diffraction grating. Baffles are provided in the entrance tubing of the monochromator to define the area of illumination on the grating. The monochromator scans in positive order, in other words anticlockwise about the pivot point in the diagram which can be varied between P and P'. The 4° offset shown was chosen to minimise the change in direction of the output beam as the grating is moved. For the range of travel of the grating, the variation is within a range of ± 0.04°. A compact four-way cross fitted on to the exit slit of the monochromator incorporates a retractable LiF window for complete rejection of higher orders when operating with $\lambda > 105$ nm, and a retractable Si photodiode for absolute flux measurements. This cross is then attached to a mirror chamber which contains an elliptical mirror and a plane mirror, thereby focussing the exit slit with 1:1 demagnification at the centre of an exit flange. This arrangement preserves the horizontal direction of the output beam, and the plane mirror can be adjusted precisely to fine tune this alignment. A capillary light guide is mounted on to the exit flange. It serves the dual purpose of bringing the light efficiently to the experimental sample and also providing an efficient vacuum differential between the experimental chamber and the mirror box.

Figure 2 shows the variation in resolution caused by defocus for the two gratings with different line spacings, and for different values of the pivot arm length. For moderate resolution and a wide choice of wavelength range, the 1200 lines/mm grating should be used. The offsets shown are the distance the exit slit needs to move from the focal distance at zero order in order to give optimum resolution over the desired wavelength range. For example, in the top component of Figure 2, the slit would be moved so that the distance GS was increased by 5.4 mm; when added in quadrature to the source size limited resolution, this results in a resolution of 0.15 nm or better over the range 80 – 280 nm. For enhanced resolution at shorter wavelengths, the 2400 lines/mm grating with an offset of 6.5 mm should be used, giving a resolution of 0.10 nm or better over the range 40 – 100 nm.

The absolute photon fluxes from the two gratings, measured at the exit slit of the monochromator, are shown in Figure 3. They are within 50% or better of the calculated values, with the high-energy grating giving slightly less flux than calculated and the medium-energy grating slightly more. The prominent peaks at short wavelength are reproduced by the calculations, and are to be expected from gratings with lamellar rulings obtained for this instrument. Second- and higher-order radiation is calculated to be less than 0.5% over the complete range of both gratings; the measured second order over the useful range of each grating is significantly greater, less than 10%. However, the LiF window can reject these components when operating with a first-order wavelength greater than 105 nm.
2.2 Apparatus for dispersed fluorescence experiments in the gas phase.

The apparatus used to perform these experiments is similar in concept to that described elsewhere [2,7]. A 120 mm$^3$ black-anodised aluminium cube is attached to the post-focusing mirror box (see Section 2.1) by a set of flexible bellows. The cube is partitioned into two separate sections divided by a 3 x 10 mm vertical slit, which can be opened or closed by a retractable plate on a vacuum-tight slider. The capillary light guide, length 330 mm and internal diameter 2 mm, ends \textit{ca.} 5 mm from this slit. Rotary-backed Pfeiffer-Blazers TPU 260 KGT and TPD 064 turbo pumps are used to evacuate the two sections. A 50 mm$^3$ brass cube is connected to the opposite face of the aluminium cube, and is separated from it by a 3.5 mm diameter aperture. This arrangement of apertures and glass capillary allows extensive differential pumping to occur, in that the operating pressure in the interaction region is \textit{ca.} six orders of magnitude higher than that in the post-focussing mirror box. Therefore, the gratings of the monochromator are preserved.

The gaseous sample is admitted from one side of the interaction region \textit{via} a needle valve. The resultant fluorescence is observed at 90° to the incident photon beam by a 0.5 m UV-grade fibre bundle containing 300 fibres attached to a Spectrosil-B window. This fibre displays > 50% transmittance in the 250 – 900 nm region, and is connected to the entrance slit of a 0.19 m Jobin-Yvon Triax monochromator. The collected signal is dispersed by one of either a UV or visible grating turret; each turret contains three gratings with 100, 300 or 1200 grooves mm$^{-1}$. The latter grating on the UV turret, which covers the 200 – 550 nm range and is blazed at 330 nm, is used for the results discussed in this paper. A 1024 x 256 pixel open-electrode CCD collects the dispersed signal, which uses liquid nitrogen cooling to reduce the dark count level to < 1 count pixel$^{-1}$ hour$^{-1}$. The standard parameters used to acquire dispersed fluorescence spectra were two accumulations with integration times of 600 s each to effect cosmic ray removal. Using longer integration times resulted in the appearance of larger quantities of cosmic rays that obscured the acquired data, even though the cosmic ray removal routines were employed throughout.

For each sample an undispersed fluorescence spectrum was also recorded, using an uncooled EMI 9883QB photomultiplier tube in place of the fibre optic and Triax/CCD detection system. The undispersed fluorescence signal was acquired as a function of photon energy by scanning the Wadsworth monochromator. Well-established data for the ionisation thresholds of each of the fluorescing states allows calibration of the gratings to occur [8]. These scans are flux normalised using the signal from a sodium salicylate window monitored on a photomultiplier tube that is inline with the incident beam. N$_2$, CO$_2$ and CF$_4$ are all gaseous samples and were used without further purification. Liquid C$_6$F$_6$ was purchased from Sigma-Aldrich with a stated purity of 99% and was subjected to several freeze-pump-thaw cycles prior to use.
3. Results

3.1 N₂

Undispersed fluorescence spectra of N₂ were recorded on both gratings over the range 18.0 – 19.5 eV, (Figure 4(a)). The optical resolution of the Wadsworth was set as 0.1 nm in both cases, corresponding to a resolution of 0.03 eV at a photon energy of 19 eV. Wavelength calibration of both gratings is performed using values obtained from these spectra. Both spectra display the same profile, with a steep rise from signal onsets at 18.75 ± 0.03 and 18.73 ± 0.03 eV for the high-energy grating (HEG) and medium-energy gratings (MEG) spectra, respectively. The signal then remains above zero for excitation energies well in excess of threshold. This shape is characteristic of non-resonant photoionisation, with fluorescence emanating from an excited state of the parent ion. The values correspond to fluorescence resulting from the N₂⁺ \( B^2 \Sigma_u^+ \rightarrow X^2 \Sigma_g^+ \) transition, starting in the \( v' = 0 \) level of the upper state [8]. Further weak onsets are observed at 19.10 ± 0.03 eV for the spectrum acquired using the HEG and 19.04 ± 0.03 eV for the MEG spectrum. Emission can now originate from the \( v' = 1 \) level of the \( \tilde{B} \) state of N₂⁺. All of these values closely match those found in previous studies using synchrotron radiation [9] and a helium lamp [10] as photon sources.

Dispersed fluorescence spectra were obtained using a 0.1 mm entrance slit on the Triax, corresponding to a resolution of 0.35 nm. Figure 5(a) shows a spectrum acquired at a photon energy of 18.96 eV on the HEG. Two peaks are observed at 391 and 428 nm, corresponding to the (0,0) and the (0,1) bands of the \( B \rightarrow X \) transition. The P-branch head and blue-degraded R-rotational envelopes of each band are readily evident, characteristic of a \( \Sigma \rightarrow \Sigma \) transition with \( B' > B'' \). This system has been rotationally resolved using electron impact [11] and synchrotron radiation [12] as the excitation sources. At photon energies greater than the \( v' = 1 \) threshold, the (1,0) and (1,2) bands also become apparent in the dispersed fluorescence spectra [13]. This effect has been observed in previous synchrotron radiation studies [12,14].

3.2 CO₂

An undispersed fluorescence spectrum of CO₂ was recorded over the 17 – 20 eV range on the HEG with a step size of 0.01 eV (Figure 4(b)). The onset of signal at 17.34 ± 0.03 eV corresponds to the energy of the \( v' = 0 \) level of CO₂⁺ \( \tilde{A}^2 \Pi_u \), emission being due to the CO₂⁺ \( \tilde{A}^2 \Pi_u \rightarrow \tilde{X}^2 \Pi_g \) transition [8]. A series of peaks is observed at higher photon energies. These have been assigned by Lee et al. [15] both to higher vibrational levels of CO₂⁺ \( \tilde{A}^2 \Pi_u \) and to Rydberg states of CO₂ which autoionise into the CO₂⁺ \( \tilde{A} \) state continuum. A substantial rise in signal is observed at 18.12 ± 0.03 eV, which corresponds to the energy of the CO₂⁺ \( \tilde{B}^2 \Sigma_u^+ \) state, with the observed emission being due to CO₂⁺ \( \tilde{B}^2 \Sigma_u^+ \rightarrow \tilde{X}^2 \Pi_g \) [8]. A dispersed
fluorescence spectrum of CO$_2^+$ is shown at an excitation energy of 18.25 eV (Figure 5(b)). The split peak observed at 289 nm is due to the $\tilde{B}^2\Sigma_u^+(000) - \tilde{X}^2\Pi_g(000)$ transition, which has high relative intensity because this transition involves negligible change in the C-O bond length. The doublet splitting of 1.24 nm or 148 cm$^{-1}$ is due to the spin-orbit splitting of CO$_2^+$ $\tilde{X}^2\Pi_g(000)$ [16,17]. This state shows a negative, inverted spin-orbit splitting, but its sign cannot be determined from our spectrum. Sets of peaks in the range 300 – 360 nm are observed, and correspond to the $\Delta v_1 = 4, 3, 2, 1, 0$ vibrational bands of the $\tilde{A} - \tilde{X}$ transition, in order of increasing wavelength [16]. A very similar spectrum was obtained using 100 eV electron impact ionisation [16] and by Penning ionisation with metastable He (2$^2$S) at 19.82 eV [18].

### 3.3 CF$_4$

Undispersed fluorescence spectra of CF$_4$ were recorded over the 10 – 26 eV range for the HEG and the 10 – 18 eV range for the MEG (Figure 6(a)). Four peaks are observed in the wider range HEG spectrum. The large peak in the 22 – 26 eV region is due to CF$_4^+$ emission, with the abrupt onset being characteristic of a non-resonant process [19]. The value of this onset, 21.70 ± 0.05 eV, matches those previously determined using photon sources [19-21] and by electron impact [22], and corresponds to the $v = 0$ level of the $\tilde{C}^2T_2$ state of CF$_4^+$. Emission is due to the $\tilde{C}^2T_2 - \tilde{X}^2T_1$ and $\tilde{C}^2T_2 - \tilde{A}^2T_2$ transitions. The peak at lowest energy, with an onset of 10.8 eV and a peak at 11.4 eV, is a lower-intensity replica of the CF$_4^+$ peak due to second-order radiation from the primary monochromator, and even reproduces the fine structure. This instrumentally-produced peak is also observed in the spectrum taken on the MEG at a much reduced level, which is consistent with the reduced flux expected at 22 eV from this grating. The peak at 13.7 eV is due to emission from the neutral CF$_3^*$ fragment. We note concurrence between the maximum values, 13.72 ± 0.03 and 13.69 ± 0.03 eV for the HEG and MEG spectra, respectively. CF$_2^*$ emission is responsible for the broad band centred at 15.9 eV. Full spectroscopic details of these CF$_3^*$ and CF$_2^*$ bands can be found elsewhere [20]. The shape of these peaks is now characteristic of a resonant process since excitation in each case is to a Rydberg state of CF$_4$, and should be contrasted with the shape of the non-resonant excitation to fluorescing electronic states of CF$_4^+$, CO$_2^+$ and N$_2^+$.

Dispersed fluorescence spectra were recorded on the HEG at $hv = 22.63$ and 13.58 eV for CF$_4^+$ and CF$_3^*$ emission, respectively. As these spectra are very similar to those recorded previously in our group [20] at the BESSY1 synchrotron, they are not shown here. The CF$_4^+$ spectrum contains two main bands at 239 and 298 nm, corresponding to the CF$_4^+$ $\tilde{C}^2T_2 - \tilde{X}^2T_1$ and $\tilde{C}^2T_2 - \tilde{A}^2T_2$ transitions, respectively. These two bands show no vibrational structure, even at enhanced resolution on the Triax, indicating the unbound nature of the $\tilde{X}^2T_1$ and $\tilde{A}^2T_2$ states [19,20,22]. A single band, centred at 237 nm, is noted in the CF$_3^*$
spectrum, due to the transition between a planar $^2 A'_1$ Rydberg state and a pyramidal ground state of $^2 A'_2$ symmetry [20]. Some vibrational structure can be resolved, even though a compromise resolution was employed due to the low intensity of this peak. All of the spectra discussed in this section are consistent with previous photon-initiated studies of CF$_4$ [19-21].

3.4 C$_6$F$_6$

Figure 6(b) displays an undispersed fluorescence spectrum of C$_6$F$_6$ recorded over the photon energy range 12 – 26 eV on the HEG. The threshold photoelectron spectrum of this molecule over the same energy range has been recorded by Dujardin and Leach [23,24]. Being singly degenerate, transitions are only observed to totally symmetric ($a_{1g}$) vibrational modes of the $\tilde{B}^2 A_{2u}$ electronic state of C$_6$F$_6^+$. Thus, transitions are only observed to the $v_1$ C-F stretch and $v_2$ ring vibration modes, whose values are quoted as 1515 and 525 cm$^{-1}$, respectively [23]. Rydberg states of C$_6$F$_6$ converging on the $C^2 B_{2u}$ state of C$_6$F$_6^+$ further complicate both fluorescence excitation and threshold photoelectron spectra. The values from our spectrum are in excellent agreement [13]. For example, the ionisation energy of C$_6$F$_6^+$ $\tilde{B}^2 A_{2u}$ ($v' = 0$) occurs at 12.595 eV [23], which agrees well with our value of 12.61 ± 0.03 eV. A dispersed fluorescence spectrum, obtained at an excitation energy of 23.24 eV, is displayed in Figure 7. This photon energy, well above the $\tilde{B}^2 A_{2u}$ state threshold, corresponds to that of maximum fluorescence signal in the C$_6$F$_6^+$ $\tilde{B}^2 A_{2u} - \tilde{X}^2 E_{1g}$ band. The two peak maxima at 462 and 473 nm correspond to the $0^0_0$ and $2^0_1$ transitions within the C$_6$F$_6^+$ $\tilde{B}^2 A_{2u} - \tilde{X}^2 E_{1g}$ electronic spectrum [18,25]. The profile of this spectrum is very similar to that produced by Penning ionisation of C$_6$F$_6$ using He (2$^1 S$) metastables [18] and is consistent with previous molecular beam work [25,26]. At our resolution, however, the effects of the dynamic Jahn-Teller distortion in the $\tilde{X}^2 E_{1g}$ ground state of C$_6$F$_6^+$, well characterised by others [27,28], are not observed. We note that the small discontinuity at 522 nm observed in this spectrum is probably an artefact of the CCD software.

4. Conclusions

We have presented the first results acquired using vacuum-UV photons from the newly-commissioned beamline 3.1 at the Daresbury SRS, namely spectra of fluorescing fragments resulting from photoexcitation of the N$_2$, CO$_2$, CF$_4$ and C$_6$F$_6$ molecules in the gas phase. Excitation spectra for each molecule were recorded, alongside the dispersed fluorescence for each of the N$_2^+$ $B^2 \Sigma_u^+ - X^2 \Sigma_g^+$, CO$_2^+$ $\tilde{A}^2 \Pi_u - \tilde{X}^2 \Pi_g$ and $\tilde{B}^2 \Sigma_u^+ - \tilde{X}^2 \Pi_g$, CF$_4^+$ $C^2 T_2 - \tilde{X}^2 T_1$ and $C^2 T_2 - \tilde{A}^2 T_2$, CF$_3^+$ $2^2 A'_2 - 2^2 A''$ and C$_6$F$_6^+$ $\tilde{B}^2 A_{2u} - \tilde{X}^2 E_{1g}$ transitions. We reiterate that such dispersed fluorescence spectra have never been
recorded routinely at the Daresbury SRS. Furthermore, although it is difficult to compare signal levels observed in the undispersed fluorescence experiments with those obtained using the Seya monochromator and a different apparatus at Daresbury, we believe that the absolute signal levels are now at least two orders of magnitude greater. Thus, the flux enhancement of the new monochromator, quantified by absolute silicon photodiode data (Figure 3), has been confirmed by these fluorescence measurements.

By exploiting the multi-channel capability of a CCD detector, the dispersed spectra were recorded on a shorter timescale than on an apparatus with a scanning grating, exit slit and photomultiplier tube. In future, a simple way of trapping out corrosive samples needs to be developed, so that a wider variety of sample molecules can be studied.

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References
**Figure Captions**

**Figure 1**: The new monochromator of Wadsworth design. G – diffraction grating; S – exit slit; C – centre of entrance flange where collimating baffles are fitted; O – vacuum chamber centre; P – pivot point, movable between P and P’.

**Figure 2**: Resolution curves, showing the effects of changing the density of rulings on the grating and the length of the pivot arm.

**Figure 3**: Absolute output fluxes from the two gratings (HEG 2400 lines/mm and MEG 1200 lines/mm), measured on a calibrated Si photodiode at the exit slit of the monochromator.

**Figure 4**: (a) Flux-normalised, undispersed fluorescence spectra of N2, measured over the 18.0 – 19.5 eV range on the HEG and MEG. Both were recorded in steps of 0.01 eV, with an integration time of 1 s and a resolution of 0.1 nm on the Wadsworth. The apparent error in the HEG plot arises due to an optical artefact of the huge strength of the signal, as illustrated by the insert. (b) Flux-normalised, undispersed fluorescence spectrum of CO2, measured over the 17 – 20 eV range on the HEG. The spectrum was recorded in steps of 0.01 eV, with an integration time of 10 s and a resolution of 0.1 nm on the Wadsworth.

**Figure 5**: (a) Dispersed fluorescence spectrum of the N2^+ B2Σ_u^+ – X2Σ_g^+ transition, recorded at 18.96 eV on the HEG with a resolution of 0.3 nm. The entrance slit of the dispersing monochromator was set at 0.1 mm. (b) Dispersed fluorescence spectrum of the CO2^+ A2Π_u – X2Π_g and B2Σ_u^+ – X2Π_g transitions, recorded at 18.25 eV on the HEG with a resolution of 0.3 nm. The entrance slit of the dispersing monochromator was set at 0.1 mm, corresponding to a resolution of 0.35 nm, or 43 cm^{-1} at 284 nm. The insert shows an expansion of the peak at 289 nm, the doublet being due to spin-orbit splitting in the X2Π_g (000) state.

**Figure 6**: (a) Flux-normalised, undispersed fluorescence spectra of CF4, measured over the 10 – 26 eV and 10 – 18 eV range on the HEG and MEG, respectively. Both were recorded in steps of 0.01 eV, with an integration time of 1 s and a resolution of 0.1 nm on the Wadsworth. (b) Flux-normalised, undispersed fluorescence spectrum of C6F6, measured over the 12 – 26 eV range on the HEG. The spectrum was recorded in steps of 0.01 eV, with an integration time of 1 s and a resolution of 0.1 nm on the Wadsworth.

**Figure 7**: Dispersed fluorescence spectrum of the C6F6^+ B2A2u – X2E1g transition, recorded at 23.24 eV on the HEG with a resolution of 0.3 nm. The entrance slit of the dispersing monochromator was set at 2 mm.
**Figure 1**: The new monochromator of Wadsworth design. G – diffraction grating; S – exit slit; C – centre of entrance flange where collimating baffles are fitted; O – vacuum chamber centre; P – pivot point, movable between P and P'.
Resolution curves, showing the effects of changing the density of rulings on the grating and the length of the pivot arm.

Figure 2
Figure 3: Absolute output fluxes from the two gratings (HEG 2400 lines/mm and MEG 1200 lines/mm), measured on a calibrated Si photodiode at the exit slit of the monochromator.
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Figure 5: (a) Dispersed fluorescence spectrum of the \( \text{N}_2^+ \, B^2\Sigma_u^+ - X^2\Sigma_g^+ \) transition, recorded at 18.96 eV on the HEG with a resolution of 0.3 nm. The entrance slit of the dispersing monochromator was set at 0.1 mm. (b) Dispersed fluorescence spectrum of the \( \text{CO}_2^+ \, A^2\Pi_u - X^2\Pi_g \) and \( B^2\Sigma_u^+ - X^2\Pi_g \) transitions, recorded at 18.25 eV on the HEG with a resolution of 0.3 nm. The entrance slit of the dispersing monochromator was set at 0.1 mm, corresponding to a resolution of 0.35 nm, or 43 cm\(^{-1}\) at 284 nm. The insert shows an expansion of the peak at 289 nm, the doublet being due to spin-orbit splitting in the \( X^2\Pi_g \) (000) state.
Figure 6: (a) Flux-normalised, undispersed fluorescence spectra of CF₄, measured over the 10 – 26 eV and 10 – 18 eV range on the HEG and MEG, respectively. Both were recorded in steps of 0.01 eV, with an integration time of 1 s and a resolution of 0.1 nm on the Wadsworth. (b) Flux-normalised, undispersed fluorescence spectrum of C₆F₆, measured over the 12 – 26 eV range on the HEG. The spectrum was recorded in steps of 0.01 eV, with an integration time of 1 s and a resolution of 0.1 nm on the Wadsworth.
Figure 7: Dispersed fluorescence spectrum of the $C_6F_6^+ \tilde{B}^2A_{2u} - \tilde{X}^2E_{1u}$ transition, recorded at 23.24 eV on the HEG with a resolution of 0.3 nm. The entrance slit of the dispersing monochromator was set at 2 mm.