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A study of the valence shell photoionisation dynamics of CH_3CN and CF_3CN

D.M.P. Holland [a,*], L. Karlsson [b]

[a] *Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK*
[b] *Department of Physics, Uppsala University, Box 530, SE-751 21, Sweden*

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Abstract

Valence shell angle resolved photoelectron spectra of CH_3CN and CF_3CN have been recorded in the photon energy range 14–120 eV, thereby allowing asymmetry parameters and branching ratios to be derived. The carbon and nitrogen K-shell photoabsorption spectra of these two molecules exhibit features ascribed to shape resonantly enhanced transitions. Energy dependent variations observed in the asymmetry parameters and branching ratios provide evidence of shape resonances influencing the valence shell photoionisation dynamics. In addition to the main lines associated with single-hole states, complex satellite structure appears in the inner valence region of the photoelectron spectrum due to many-electron effects. The experimental spectra have been interpreted using previously reported ionisation energies and spectral intensities obtained from Green's function calculations.

Keywords: Photoelectron spectroscopy; Photoionisation dynamics; Electronic interactions

1. Introduction

Probably the best understood example of shape resonant phenomena [1,2] influencing molecular photoionisation dynamics occurs in nitrogen, N≡N, where rapid, energy dependent, variations have been observed in experimental parameters, such as photoabsorption cross-sections, photoelectron angular distributions and branching ratios. The nitrogen K-shell photoabsorption spectrum [3] is dominated by a prominent peak 9 eV below the ionisation edge and a broad feature 9 eV above threshold. An interpretation of this core level absorption structure was first proposed by Dehmer and Dill [4]. Their theoretical work showed that the peak observed in the discrete part of the spectrum should be attributed to the shape resonantly enhanced N 1s → $2\pi_g$ transition and that the feature lying in the continuum resulted from a shape resonance in the σ_u channel. Subsequent theoretical [5] and experimental [6] investigations studied the effect of the σ_u shape resonance on the nitrogen K-shell photoelectron angular distributions.

In vibrationally resolved photoelectron spectra, shape resonances induce vibrational state dependent asymmetry parameters and non-Franck-Condon branching ratios. Such effects have been predicted [7–10] and verified experimentally [11,12] for the N_2 $3\sigma_g$ orbital. As a result of these extensive investigations, the influence of the σ_u shape resonance on the core and valence shell photoionisation dynamics has been thoroughly examined and characterised.

Past work on molecular photoionisation has demonstrated that many of the prominent features attributable to shape resonant phenomena in the total or partial photoionisation cross-sections or in the photoelectron angular distributions can be interpreted successfully within the independent particle model by applying dipole selection rules to identify which molecular orbitals couple to specific shape resonantly enhanced channels [1,2]. Absorption features associated with such transitions are generally easier to identify in core level spectra, where the number of allowed transitions is usually small, than in valence shell spectra. When these identifications can be made, term values may be derived for specific shape resonantly enhanced transitions from the core level spectra. These term values can then be used to estimate the positions of the corresponding valence shell shape resonances after taking into account the shift by a few eV

* Corresponding author. Tel.: +44 1925 603 425; fax: + 44 1925 603 124.
E-mail address: d.m.p.holland@dl.ac.uk (D.M.P. Holland).

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towards higher kinetic energy, due to differences in screening. This procedure has been applied successfully to many small polyatomic molecules [1] and has allowed shape resonantly induced energy dependent variations in valence shell experimental parameters to be assigned.

The principle features occurring in the carbon and nitrogen K-shell photoabsorption spectra of hydrogen cyanide H–C≡N [13], cyanogen N≡C–C≡N [13], methyl cyanide $\begin{matrix} H \\ H-C-C\equiv N \\ H \end{matrix}$ [14] and trifluoroacetonitrile $\begin{matrix} F \\ F-C-C\equiv N \\ F \end{matrix}$ [15] are similar to those in the N_2 K-shell spectrum. In each molecule, the discrete part of the spectrum exhibits a single intense peak ascribed to a shape resonantly enhanced transition into a π* orbital and the ionisation continuum displays a broad peak due to a transition into a σ* orbital. (Note that the K-shell spectra of CF_3CN have been recorded only below the ionisation edges.) These similarities suggest that investigations on small polyatomic molecules containing a C≡N group represent a natural progression in the study of shape resonant phenomena. Valence shell photoelectron studies have already been performed on hydrogen cyanide [16,17], cyanogen [18–20], methyl cyanide [21], cyanoacetylene [22] and the cyanogen halides [23]. However, the experimental verification of the predicted shape resonances [16,18,20,22–25] in these C≡N containing molecules has been patchy.

Of these molecules, the most comprehensively studied is cyanogen, where the carbon K-shell absorption spectrum exhibits features having term values of 8, −12 and −19 eV which have been ascribed to shape resonantly enhanced transitions into the $2\pi_u$, σ^*_{CN} or σ^*_{CC} orbitals, respectively [13]. Lynch et al. [25] have investigated the valence shell photoionisation dynamics theoretically, and their work suggests that shape resonant trapping arises from both the CN components and from the C–C bond. According to their calculations a σ_u shape resonance, associated with the C–C bond, occurs at a photoelectron kinetic energy of ∼2.5 eV, whilst the σ_g and σ_u shape resonances, associated with the CN groups, occur at energies of ∼18 and 27 eV, respectively. In addition, a shape resonance in the π_u channel was identified at ∼20 eV. The predictions of Kreile et al. [18] are broadly similar but the π_u shape resonance was not found. However, their calculations suggested that a resonance occurred in the π_g channel at a kinetic energy of ∼3 eV. Several of these predicted shape resonances have been observed [19,20], although the calculated and measured locations sometimes differ by a few eV.

Holland et al. [21] have searched for the effect of shape resonances on the valence shell photoionisation dynamics of methyl cyanide by measuring vibrationally resolved photoelectron asymmetry parameters and branching ratios for the $(2e)^{-1}$ $\tilde{X}^2E$ and $(7a_1)^{-1}$ $\tilde{A}^2A$ states. No evidence of resonant phenomena was obtained in the photon energy range (13–24 eV) covered in that work, and this led to the suggestion [21] that shape resonances might not affect the valence shell photoionisation dynamics of CH_3CN until higher excitation energies. At that time the inner shell photoabsorption spectra of methyl cynanide, which could have provided estimates for the positions of the shape resonances, had not been measured. These spectra have now been recorded by Hitchcock et al. [14] and features associated with transitions into the 3e(π*) or σ^*_{CN} orbitals are observed ∼5.5 eV below, and ∼16 eV above, the ionisation edges, respectively. In addition, the carbon 1s spectrum exhibits a peak ascribed to transitions into the σ^*_{CC} orbital ∼2 eV below threshold. Similarly, peaks assigned to transitions into π^*_{CN} or σ^*_{CC} orbitals have been observed ∼6 and 3 eV, respectively, below threshold in the carbon K-shell spectrum of CF_3CN [15]. Thus, the principle features occurring in the carbon and nitrogen K-shell photoabsorption spectra of these C≡N containing molecules are similar.

In the present work, valence shell photoelectron spectra of CH_3CN and CF_3CN have been measured between threshold and 120 eV, thereby allowing asymmetry parameters and branching ratios to be derived. Particular attention has been focussed on the structure observed in the inner valence region where the molecular orbital model of ionisation breaks down [26]. The valence shell electronic configuration of CH_3CN is well established [27,28] and may be written as (using C_{3v} symmetry)

$$(4a_1)^2(5a_1)^2(6a_1)^2(1e)^4(7a_1)^2(2e)^4$$

However, that for CF_3CN remains uncertain. In the present study, the configuration calculated by Åsbrink et al. [29] has been adopted

$$(5a_1)^2(2e)^4(6a_1)^2(7a_1)^2(8a_1)^2(3e)^4(4e)^4(5e)^4(1a_2)^2$$
$$(9a_1)^2(6e)^4(10a_1)^2$$

although our experimental data do not allow this configuration to be distinguished from that calculated by Shimizu et al. [30] where an ordering of $(9a_1)^2(1a_2)^2(10a_1)^2(6e)^4$ was obtained for the outer orbitals. The HeI and HeII excited photoelectron spectra of CH_3CN [28,31–34] and CF_3CN [29,35] have been recorded previously and these have enabled vibrational structure to be observed in some of the bands associated with the outer valence orbitals.

2. Experimental apparatus and procedure

The photoelectron spectra were recorded using a rotatable hemispherical electron energy analyser and synchrotron radiation emitted by the Daresbury Laboratory storage ring. Detailed descriptions of the monochromator [36] and the experimental procedure [37] have been reported.

The photoionisation differential cross-section in the electric dipole approximation, assuming randomly oriented targets and electron analysis in a plane perpendicular to the photon propagation direction, can be expressed in the form

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{total}}{4\pi}\left[1 + \frac{\beta}{4}(3P\cos 2\theta + 1)\right],$$

where σ_{total} is the angle integrated cross-section, β the photoelectron asymmetry parameter, θ the photoelectron ejection angle relative to the major polarisation axis and P is the degree of linear polarisation of the incident radiation. At each photon energy, photoelectron spectra were recorded at $\theta = 0$ and 90°, thus allowing the asymmetry parameter to be determined