Photoelectron Spectroscopy using Pulsed Free Jets*

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Abstract

The use of pulsed gaseous free jets in the study of atomic and molecular species by ultraviolet photoelectron spectroscopy (UPS) offers a number of advantages over the usual continuous flow room temperature technique. Pulsed free jet expansions provide, on the one hand, 'cold' molecules for which spectroscopy is simplified through the absence of hot band structure and, on the other hand, cluster species including dimers, trimers and higher clusters, as well as intermolecular species, all generally of low intermolecular binding energies. Furthermore a high pressure gas pulse is a suitable medium for the preparation, relaxation and transport of reactive species formed in processes such as pyrolysis, photodissociation or electrical discharge. This paper describes the modifications made to an ultraviolet photoelectron spectrometer to allow measurements on pulsed free jet expansions. The important features of the modified instrument concern the control of the gas beam and the timing electronics for photoelectron detection. Examples of He I photoelectron spectra presented include (*a*) the demonstration of hot band structure in the room temperature UPS of ammonia, (*b*) the preparation of the dimer $(NO)_2$ and higher clusters $(NO)_n$ of nitric oxide, (*c*) the UPS of sulfur dioxide clusters $(SO_2)_n$, and (*d*) the UPS of ammonia clusters $(NH_3)_n$.

1. Introduction

The measurement of ultraviolet photoelectron spectra (UPS) of gas-phase atoms and molecules has normally involved a continuous flow of gas (at room temperature) into the ionisation region where, typically, collimated He I and He II radiation is used for ionisation (Rabalais 1977). In the case of organic solids, elevated temperatures are utilised in a heated inlet system to provide sufficient vapour pressure, allowing measurement at acceptable photoelectron count-rates. Some workers have used lower temperatures for UPS studies, specifically in the case of the dimers of carboxylic acids (Thomas 1972).

While a continuous gas flow is applicable to the routine study of stable molecules, the use of a pulsed gas source is a convenient means of preparing many interesting chemical species for study by UPS.

Molecular beams formed by expansion of a high pressure gas through a small nozzle are being used increasingly in many areas of spectroscopy. The prototype molecular

beam is a continuous one which usually requires a number of stages of differential pumping prior to the intersection of the beam with radiation in a spectroscopic experiment. For photoelectron studies the local pressures encountered by electrons in flight toward an electron energy analyser must be, in the high vacuum regime, no higher than 10^{-3} Torr (1 Torr = 133 Pa). A skimmed and collimated molecular beam contains a relatively small fraction of the gas used in producing it, and while the vapour pressure at the centre of the beam is relatively high, above 1 Torr near the nozzle, the average pressure in the region traversed by the photoelectrons is relatively low. However, at a point of ionisation relatively distant from the nozzle, which is usual when a skimmer and collimator are used, the photoelectron count-rate is consequently rather low.

Free jet expansions are being used in various spectroscopic applications, but while they offer a simpler and cheaper alternative to a differentially pumped molecular beam as a source of 'cold' molecules, they normally produce a relatively high average pressure. This offers no impediment to measurements of, say, fluorescent emission, or other optical properties, but can be a problem for photoelectron transmission. In order to achieve a high degree of expansive cooling in a free jet expansion, a large stagnation pressure is required and if a typical nozzle size of around 0·1 mm diameter is used, a large chamber and high capacity vacuum pumping are required to maintain the operating pressure in the chamber below 10^{-3} Torr.

The pulsed free jet offers a compromise which, while it is technically more difficult to produce and control, has the advantage of requiring only moderate pumping capacity in a small chamber. A high degree of expansive cooling is achieved with large stagnation pressures generating the gas beam. By varying the duty cycle of the gas pulsing control, a stagnation pressure and an average chamber pressure can be chosen which are adequately handled by a single moderate pumping system. So a stagnation pressure of 1 atm (101 325 Pa) with a 0·1 mm diameter nozzle operating at a 5% duty cycle, say 1 ms pulses at a repetition rate of 50 Hz, gives an average chamber pressure of 10^{-4} Torr using a 6 in. (15·24 cm) diffusion pump (500 L s^{-1}) backed by a 6 L s^{-1} rotary pump.

There are two main features of a pulsed gas inlet system which can be exploited in spectroscopic studies. First, the low vibrational and rotational temperatures achieved in the expansion, particularly of a seeded gas (a dilute mixture in, for example, helium), provide 'cold' molecules with spectra simplified through the reduction of 'hot' bands arising from the Boltzmann distribution of vibration–rotation states at room temperature. As well, the expansion allows cluster formation particularly for neat or concentrated gas mixtures, so that under appropriate conditions atomic and molecular dimers can be obtained in sufficient abundance for spectroscopic study. Higher clusters can also be produced.

Second, the high stagnation pressure region is suitable for the preparation, relaxation and transport of reactive species such as radicals, metal clusters and intermolecular species. The production of metal clusters by laser vapourisation of metals followed by supersonic expansion involving clustering control has recently been demonstrated (Rohlfing *et al.* 1984; Geusic *et al.* 1985). Radical species prepared by pyrolysis, photodissociation or electrical discharge in a high pressure carrier gas undergo rapid vibrational relaxation. They can be maintained and transported free of reactive wall collisions and following free jet expansion can be studied by various means.
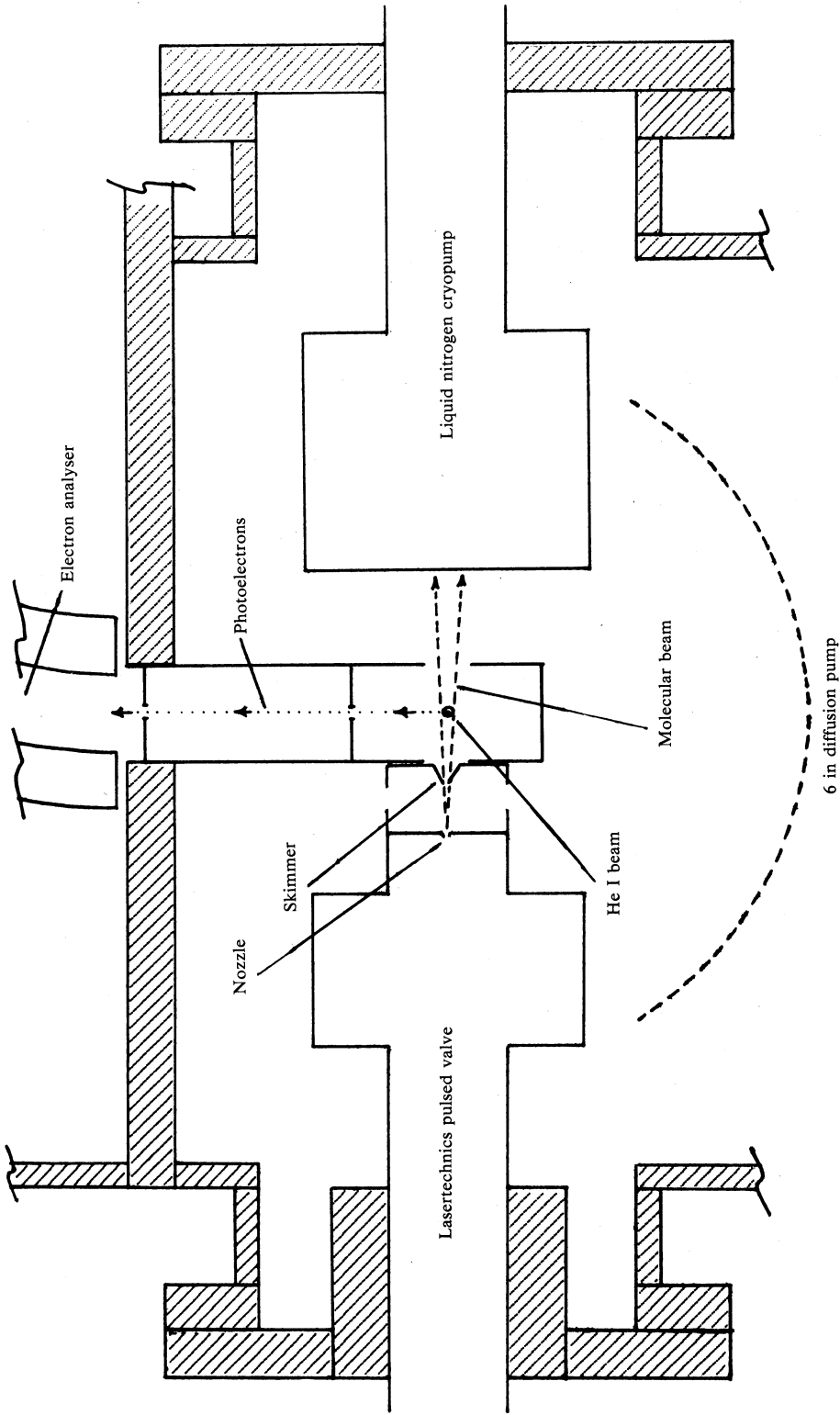
Fig. 1. Gas inlet system for u.v. photoelectron spectrometer modified for use with pulsed gases.

2. Techniques

The required modifications to the typical u.v. photoelectron spectrometer involve the addition of pulsing and timing circuitry, to operate for and with the gas pulsing mechanism, and the incorporation of an appropriate skimmer or collimator and a beam catcher or stopper, to provide a suitable pulsed molecular beam intersecting the collimated He I u.v. beam.

We have made these modifications to our double-chamber u.v. photoelectron spectrometer which has been used in a variety of measurements of He I and He II photoelectron spectra since its construction in 1976. The modifications have been achieved without any upgrading of the pumping system which includes a 6 in. (15·24 cm) diffusion pump on the gas sample chamber and a 4 in. (10·16 cm) diffusion pump on the electron analyser chamber. The spectrometer, which has been described in previous reports (Carnovale 1980; Livett 1983), incorporates a double hemispherical electron analyser and is controlled by an Apple IIe microcomputer which drives the analyser in a multi-channel multiple-sweep mode and stores, adds and adjusts the digitised spectrum according to a preset ionisation energy (IE) range, drift tolerance, and total accumulation time.

The modifications to the gas sample chamber are illustrated in Fig. 1. A Lasertechnics pulsed valve (LPV) replaces the usual continuous flow gas inlet of the gas sample chamber. This valve is designed around a vibrating piezoelectric crystal. The assembly consists of a thin disc bimorph (two crystals sealed to a thin nickel separating disc) with a light Viton-tipped aluminium poppet extending from its centre (Cross and Valentini 1982). A high voltage d.c. pulse drives the poppet away from the small diameter nozzle outlet allowing gas flow until the voltage is removed, after which the poppet relaxes, closing the valve. The driver circuitry provides a pulsewidth of 100 μs upwards to fully open, and a repetition rate from 0 to 250 Hz. This allows for duty cycles varying over the complete range of 0–100%, and so can be used with a vacuum pumping system of any capacity. The reproducibility of the gas pulse characteristics is reasonably good. However, by gating for photoelectron detection over a chosen period slightly narrower than the gas pulsewidth, any variations in the pulse shape at its rise and fall have no serious effect. In this case the reproducibility of the pulse height is important. While numerous gas pulses provide data for each channel in the photoelectron spectrum there is no obvious effect on the *S/N* ratio due to this factor.

The skimmer used to collimate the free jet gas pulse serves to reduce the local pressure in the region of photoelectron travel between the He I beam and the analyser entrance slits. Most of the gas deflected from the skimmer finds its way into the throat of the diffusion pump and the region beyond the skimmer in the ionisation box is of acceptably low pressure. This region is also 'protected' by a liquid-nitrogen cryopump. This acts as a beam catcher for the gas after it has passed through the ionisation box. The cryopumping efficiency is capable of reducing the average chamber pressure by a factor of 10 under the usual operating conditions and, as expected, works well with readily condensible gases.

A newly installed ETP multi-dynode electron multiplier operates continuously, and its preamplified output is gated using a window with preset delay and open times activated by the synchronous output pulse of the LPV driver control. The computer program sets the photoelectron energy channel, then delivers a pulse to open the gas

valve. The preset gas pulse-width and electron pulse counting delay and window allow the accumulation of photoelectron counts in the appropriate channel during the chosen part of the gas pulse.

3. Applications

Where the photoelectron spectra indicate the presence of cluster species these are normally of relatively low concentration. Analysis using spectrum stripping or subtraction techniques is used to obtain enhanced spectra of the species of interest. These procedures require that spectra of different mixtures be obtained under closely similar experimental conditions and be of high signal-to-noise characteristics. Experience has shown that the reliability of spectrum stripping exercises often depends on features peculiar to each case (Carnovale 1980; Livett 1983).
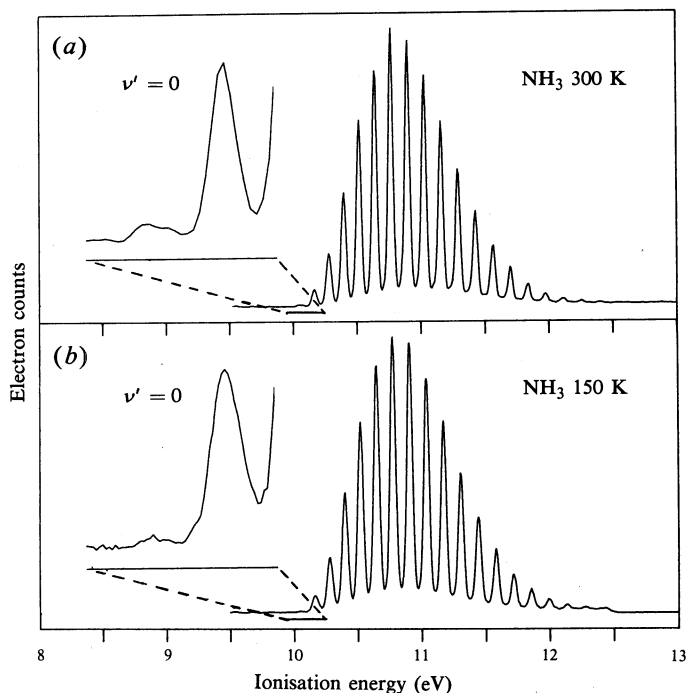

Fig. 2. He I photoelectron spectra of NH_3 at (*a*) room temperature (300 K) with conventional gas inlet and (*b*) reduced temperature (150 K) in a pulsed free jet expansion. The full scale of each frame represents 30 000 counts.

(a) Ammonia

The room temperature He I UPS of NH_3 has a highly structured first band which, since it was first measured, has been considered to be affected by hot band structure visible at the low IE onset of the band (Rabalais *et al.* 1973). The spectrum obtained using a pulsed source with an estimated vibrational temperature of 150 K is compared
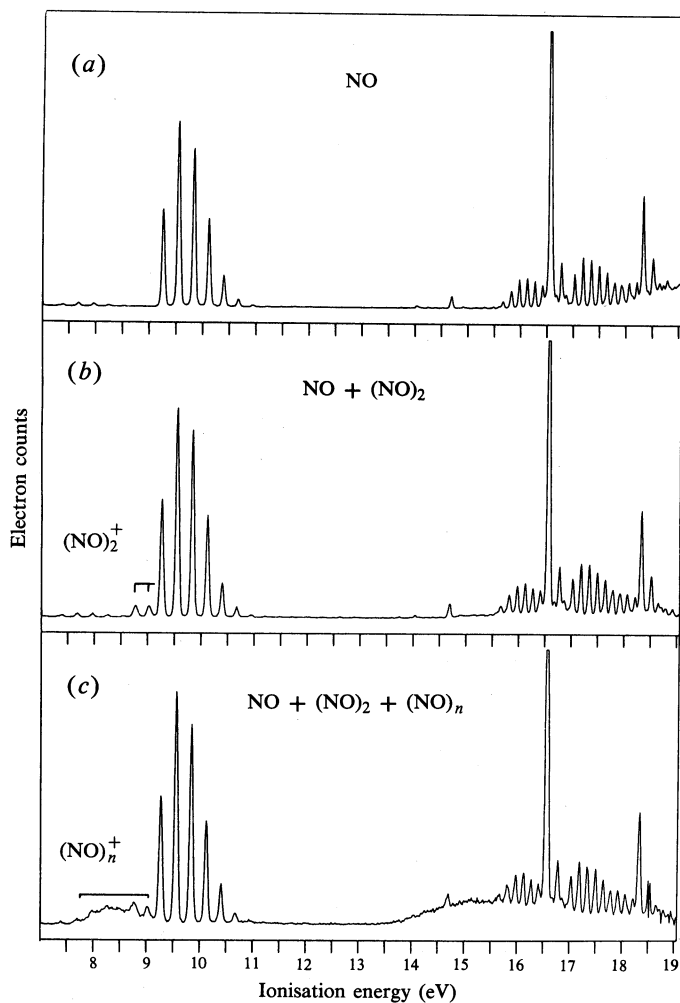
Fig. 3. He I photoelectron spectra of NO: (*a*) for monomer NO; (*b*) from a pulsed source at a stagnation pressure of 350 kPa (NO/He = 0·1), showing the presence of dimer $(NO)_2$; (*c*) from a pulsed source at a stagnation pressure of 650 kPa (NO/He = 0·1), showing the presence of higher clusters $(NO)_n$. The full scale of each frame represents 20 000 counts.

in Fig. 2 with a typical spectrum obtained with a near room-temperature gas. The weak peak at 10·08 eV is 0·14 of the intensity of the $v' = 0$ peak at 10·19 eV in the 300 K spectrum of Fig. 2*a*, but is reduced to 0·07 of the $v' = 0$ peak at 150 K in Fig. 2*b*. The adiabatic IE for the process $NH_3 \rightarrow NH_3^+ + e$ is clearly shown to be 10·19 eV. The two spectra show slightly different peak shapes arising from variations in rotational populations as well as instrumental effects relating to the different experimental conditions. While the number of electron counts measured for the $(v'' = 1) \rightarrow (v' = 0)$ 'hot' lines are relatively small, the structure is further enhanced in spectra measured at higher temperatures (T above 300 K).
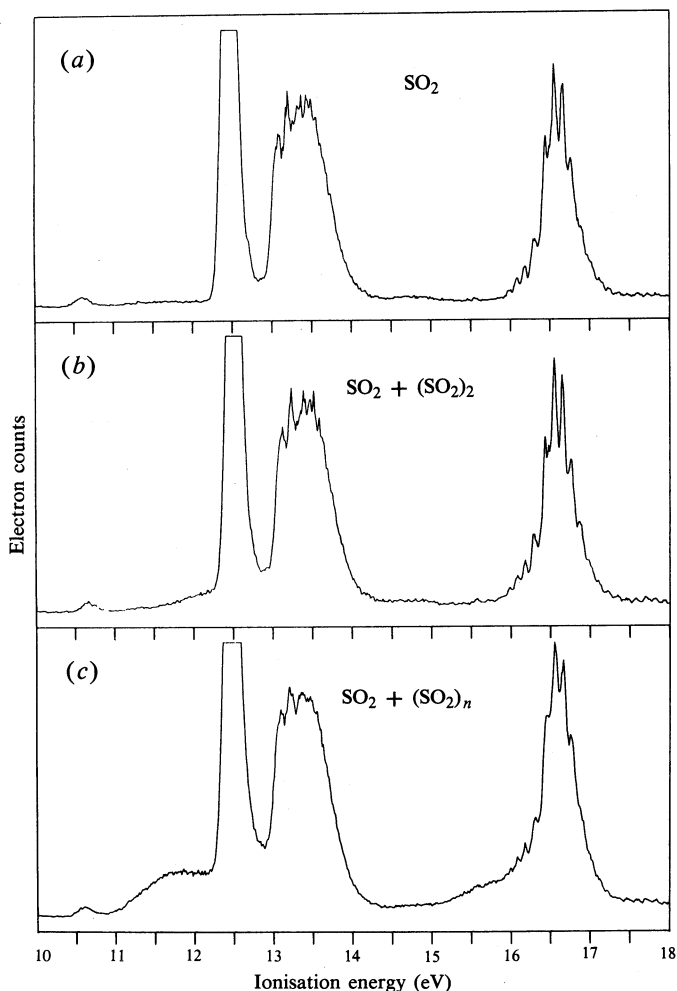
Fig. 4. He I photoelectron spectra of SO_2: (*a*) for monomer SO_2; (*b*) from a pulsed source ($0 \cdot 1$ mm sonic nozzle) at a stagnation pressure of 140 kPa ($SO_2/He = 0 \cdot 1$), showing the presence of dimer $(SO_2)_2$; (*c*) from a pulsed source ($0 \cdot 1$ mm conical nozzle) at a stagnation pressure of 140 kPa, showing the presence of higher clusters $(SO_2)_n$. The first band of SO_2 is truncated at approximately 50% of its maximum height for illustrative purposes. The full scale of each frame represents 5000 counts.

(b) Nitric Oxide Dimer

   The N–N bond in N_2O_2 is so weak that N_2O_2 is regarded as the dimer $(NO)_2$ of the observed room temperature radical species NO. The pulsed beam of NO provides an estimated vibrational temperature of 50 K, which allows formation of $(NO)_2$ and higher clusters. The He I spectra shown in Fig. 3 compare the normal spectrum of NO (Fig. 3*a*) with spectra of NO/He gas mixtures (NO/He $= 0 \cdot 1$) obtained at stagnation pressures of 350 kPa (Fig. 3*b*) and 650 kPa (Fig. 3*c*). The gas mixture of Fig. 3*b* contains about 3% of NO in the dimeric form. The $v' = 0$ and $v' = 1$ peaks of the first band of $(NO)_2$ are shown at $8 \cdot 77$ and $9 \cdot 02$ eV in excellent agreement with
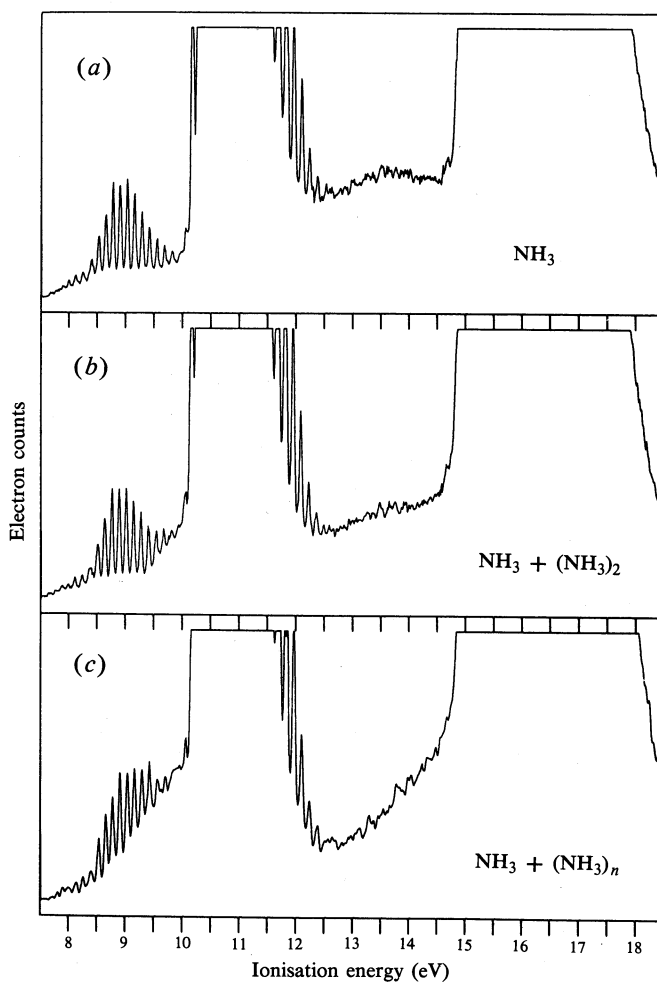
Fig. 5. He I photoelectron spectra of NH_3: (*a*) for monomer NH_3; (*b*) from a pulsed source (0·1 mm sonic nozzle at 47°C) at a stagnation pressure of 50 kPa, showing presence of dimer $(NH_3)_2$; (*c*) from a pulsed source (0·1 mm sonic nozzle at 15°C) at a stagnation pressure of 100 kPa, showing presence of higher clusters $(NH_3)_n$. The spectra are truncated at approximately 5% of the first NH_3 band maximum. The full scale of each frame represents 4000 counts.

photoionisation efficiency data (Ng *et al.* 1977; Linn *et al.* 1981). Higher clusters of NO are revealed in the gas mixture giving the spectrum in Fig. 3*c*. The spectrum of the mixed clusters is similar to that measured for condensed NO (Kao *et al.* 1984).

Spectrum stripping allows the derivation of spectra assigned as that of the dimer $(NO)_2$ and mixed clusters $(NO)_n$ where $n \geqslant 3$ (Carnovale *et al.* 1986*a*).

(c) Sulfur Dioxide Clusters

The pulsed jet He I spectrum shows that SO_2 is susceptible to clustering under relatively moderate conditions. With increased stagnation pressure, corresponding to reduced gas beam temperature, there is a steady increase in average cluster size which is indicated by a steady decrease in the IE onset below that of the first monomer band

at $12 \cdot 2$ eV. Fig. 4 includes the monomer spectrum (Fig. $4a$), a spectrum obtained at 140 kPa stagnation pressure ($0 \cdot 1$ mm sonic nozzle) and considered to include that of the dimer with an onset at $11 \cdot 7$ eV (Erickson and Ng 1981), and a third spectrum obtained using 140 kPa stagnation pressure but with a $0 \cdot 1$ mm conical nozzle, and showing a lower ionisation onset around $11 \cdot 0$ eV due to the presence of higher clusters.

Spectrum stripping provides a spectrum representative of the dimer species $(SO_2)_2$ and a spectrum for a mixture of clusters $(SO_2)_n$ where $n \geqslant 2$ (Carnovale et al. 1986b). The latter spectrum is similar to that of condensed SO_2 (Campbell et al. 1982).

(d) Ammonia Dimer

At low temperature in a pulsed source, NH_3 is subject to considerable clustering. Using a heated nozzle, the proportion of dimer can be optimised in a gas mixture which contains a negligible amount of higher clusters. Fig. 5 compares the monomer spectrum of NH_3 (Fig. $5a$) with that of a mixture containing about $0 \cdot 5\%$ of the dimer $(NH_3)_2$ (based on the assumption that the dimer cross section is twice that of the monomer, Fig. $5b$) and that of a mixture containing higher clusters (Fig. $5c$). A prominent feature of these spectra is the He Iβ first band of NH_3 ($\sim 2\%$ of He Iα intensity) which is situated at 8–10 eV on the He Iα ionisation scale. The relative intensities of the He Iα low IE band of the dimer and clusters can be gauged against this weak He Iβ monomer band.

The stripped spectra (Carnovale et al. 1986c) show that $(NH_3)_2$ has a first band onset at $9 \cdot 4$ eV and a maximum (vertical IE) at $10 \cdot 1$ eV. By comparison, monomer NH_3 has $I_a = 10 \cdot 19$ eV and $I_v = 10 \cdot 78$ eV indicating that the dimer band is only slightly broader. The mixed clusters show a broader first band with onset $8 \cdot 8$ eV and maximum $9 \cdot 96$ eV, which can be compared with that obtained for condensed NH_3 (Campbell et al. 1982).

4. Conclusions

The use of pulsed free jet expansions in photoelectron spectroscopic studies provides access to molecular species not available with a conventional gas inlet system. These include vibrationally 'cold' molecules, molecular dimers, atomic and molecular clusters, and intermolecular species, as well as short-lived radical species. This paper has described examples of some of these systems, and it is anticipated that examples of others will be forthcoming.

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