Improved Vacuum Ultraviolet Supersonic Jet Absorption Spectrometer

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We report on design changes that have significantly improved the performance of our supersonic jet ultraviolet and vacuum ultraviolet absorption spectrometer. We incorporated the following three features: (1) direct detection of VUV photons rather than scintillator detection; (2) a triple-pass mirror arrangement; and (3) a larger-pathlength monochromator and a finer grating. These upgrades have yielded about an order-of-magnitude improvement in sensitivity and greater than fivefold improvement in resolution.

Index Headings: **Instrumentation, molecular beam; Spectroscopic techniques; UV-visible (VUV) spectroscopy.**

INTRODUCTION

Direct absorption spectroscopy in supersonic jets has proved very important for recording high-resolution spectra in the absence of thermal broadening and congestion.[1–10] Several designs incorporate laser excitation to achieve much narrower absorption linewidths over a limited tuning range.[1–3] An alternative approach is to use a dispersed incoherent light source to achieve broader tunability, but at somewhat lower resolution than for laser excitation.[4–10] This trade-off is worthwhile for less commonly studied molecules for which medium-resolution "survey" spectra over large wavelength ranges are desirable. This objective motivated us to design a spectrometer that would operate over a spectral range extending from the visible to energies exceeding the ionization potential of most molecules.[9,10] In a previous paper we reported on an ultraviolet (UV)/vacuum ultraviolet (VUV) supersonic jet absorption spectrometer and provided a demonstration of its capabilities.[9] We also made a number of suggestions for improving resolution and sensitivity. In this paper, we report on the implementation of a few key upgrades that have yielded significant improvements in performance.

EXPERIMENTAL

A schematic of the new apparatus is given in Fig. 1. The vacuum apparatus has been described previously,[9,10] so we will present a brief description and focus mostly on those features that have been added since we last reported on the apparatus in this journal.[9] A gas mixture consisting of sample vapor in a high pressure of inert carrier gas (e.g., He, Ar) is introduced into the vacuum chamber by a pulsed nozzle that operates at 50 Hz and has an open time that can be varied from 200 to 1000 μs. Because these absorption experiments use a continuous output light source, it is advantageous to maximize the gas pulse width within the limits of the pumping capacity. A desired sample pressure is achieved in a number of ways, depending on the volatility of the sample. Gas-phase samples (e.g., NH_3) are pre-mixed with the carrier gas in a high-pressure cylinder. Low-boiling-point liquid samples (e.g., hydrazines, CH_3I) are placed in a cooled bubbler through which carrier gas flows. Low-vapor-pressure liquid and solid samples are placed directly in the pulsed valve housing, which is fitted with temperature-controlled heaters for raising sample vapor pressure. Absorption spectra are recorded by measuring the light source intensity by photon counting over two time windows, one that is coincident with the gas pulse (I) and one that precedes it (I_0).[9,10] The upgrades most recently added to the apparatus are described below.

Monochromator. We have replaced the original 0.2-m Seka-Namioka-type monochromator (40-Å/mm dispersion with a 1200-lines/mm grating) with a 0.5-m Czerny-Turner-type monochromator (16- and 5-Å/mm dispersion, respectively, with a 1200- or 3600-lines/mm grating). Our apparatus can achieve 1–2 cm^{-1} resolution at 200-nm excitation with a 10-μm slit width.

Photon Counting. In our previous apparatus, we relied on conversion of VUV photons to the near-UV/visible region by coating the exit window for the light beam with sodium salicylate, which acted as a scintillator. We now employ solar-blind photomultiplier tubes (PMTs) to detect VUV photons directly. We have gained about a factor of 5–10 sensitivity by detecting the direct light beam rather than the diffuse scintillator emission. Depending on the spectral tuning range of interest, we use either a Hamamatsu R1259P (115–195 nm, 120-nm peak) or a R1259 (115–320 nm, 190-nm peak) PMT. The use of a short-wavelength-sensitive detector also diminishes the need to shield the apparatus from room lights.

Triple-Pass Cell. The addition of two mirrors, as shown in Fig. 1, effectively increases the absorbance by a factor of three. The mirror substrates (0.20 × 0.20 × 0.62 in. quartz) were aluminum coated with a MgF_2 overcoat. This particular coating, which extends to 120 nm, is designated as #1200 by Acton Research Corporation. The mirrors were separated by about 2 cm and were canted by about 15%, as indicated in Fig. 1. The quality of the reflectors deteriorated over an extended period of time when used with jet-expansions of hydrazines and CH_3I. The reflectivity decreased by a factor of two per mirror after about 100 h of operation. The durability was greater for use with NH_3. We have not tested it for other mol-

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ecules. The surfaces cannot always be cleaned to restore reflectivity, so several backup mirrors are kept in stock.

RESULTS AND PERFORMANCE

Sensitivity. Improvement in sensitivity was made by two means: increasing sample absorption $(I_0 - I)/I_0$ by including the triple-pass reflectors, and improving the minimum detectable value of absorption by increasing the detected light intensity and the overall signal-to-noise ratio (S/N). The triple-pass reflector increases absorption and, ideally, sensitivity by a factor of three; however, because of losses due to incomplete reflection, the statistical noise level (see below) increases as well. In the worst case, only 50% of the original light beam is detected, which increases the noise level by a factor of $\sqrt{2}$. The increase in S/N is therefore, by a factor between two and three.

The minimum detectable absorption signal, $S_{min} = [(I_0 - I)/I_0]_{min}$, is a function of the S/N of I_0 and I, which is given by $\sqrt{\text{counts}}$. The count rate is a function of λ and the monochromator resolution $\Delta\lambda$, which we denote as $C(\lambda, \Delta\lambda)$. The minimum detectable absorption is approximately

$$S_{min} = 2^{1/2}[C(\lambda, \Delta\lambda) \cdot n \cdot \tau_{gate}]^{-1/2}$$

where τ_{gate} and n are the counting gate width and the number of pulses per point, respectively.[9] The factor of $\sqrt{2}$ accounts for the sum of the noise levels for I_0 and I. An increase in $C(\lambda, \Delta\lambda)$ has been achieved in two ways: by directly counting VUV photons using a solar-blind PMT, and by improving the monochromator light throughput. The first upgrade accounts for up to an order-of-magnitude increase in counting efficiency. The second upgrade involves using a higher-resolution monochromator grating (3600 lines/mm). Experimental resolution is adjusted by varying the monochromator slit width, sw. However, this step has a strong effect on count rate since light throughput is approximately proportional to $(sw)^2$ (assuming linear attenuation at each slit). Because $\Delta\lambda \propto sw$, count rate is related to resolution by the relation $C(\lambda, \Delta\lambda) \propto (\Delta\lambda)^2$. A more finely ruled grating increases dispersion to increase resolution. Though light throughput through the exit slit is inversely proportional to grating dispersion (resolution), the overall light throughput is effectively greater because the entrance and exit slits can be operated at larger widths. The overall effect is that for a specified resolution $\Delta\lambda$ the value of $C(\lambda, \Delta\lambda)$ increases linearly with grating resolution.

Although sensitivity has been improved by increasing the count rate, an excessive count rate can lead to counting error due to the limiting pulse pair resolution of the PMT/photon counting detection system (current, $\tau_{res} =$ 10 ns). The probability of a counting error due to two closely spaced pulses being detected as one pulse is $C \times \tau_{res}$. An acceptable count rate is 10^6 counts/s, which limits counting error to 1%. For typical conditions of $\tau_{gate} = 1$ ms, and a 50-Hz repetition rate, a detection sensitivity of $S_{min} = 0.001$ is achieved for a signal averaging time of 20 s per spectral point. Increasing C to 10^7 counts/s reduces the averaging time to 6 s, but increases the intensity uncertainty to 10%, which may be an acceptable trade-off for certain situations. Because of the limiting count rate condition for achieving accurate intensity measurements, the benefits of improved detection efficiency are obtained by extending some specified sensitivity to higher spectral resolution.

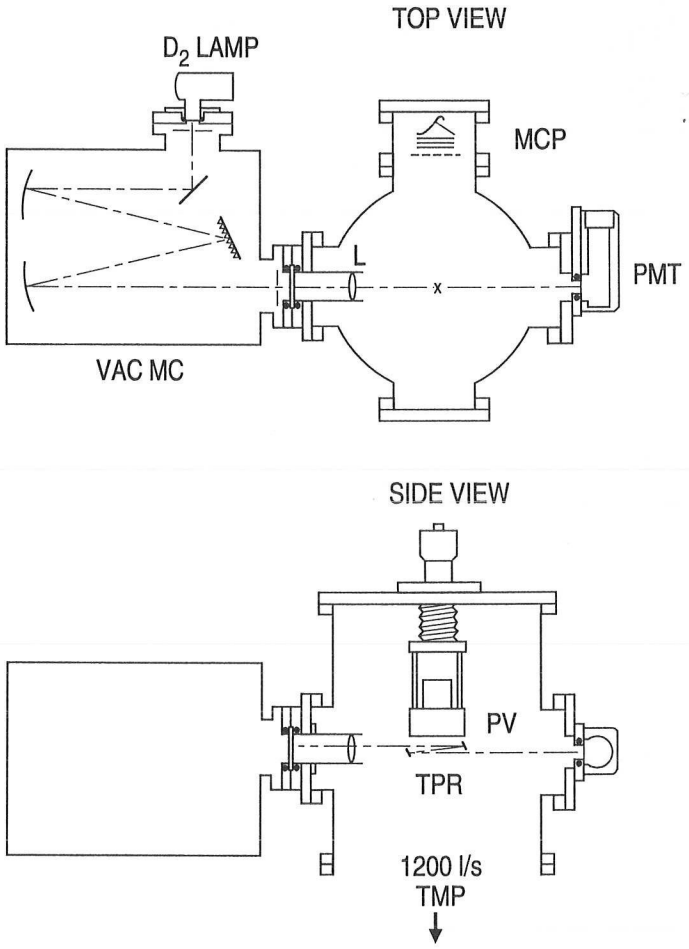

FIG. 1. Diagram of the supersonic-jet VUV absorption spectrometer. The × marks the crossing of the molecular jet and the light beam. The pulsed valve (**PV**) is at the top of the chamber, and the gas output is directed into the turbomolecular pump (**TMP**). The photomultiplier tube (**PMT**) assembly translates down (side view) to accommodate the displacement of the light beam by the triple-pass reflector (**TPR**). The vacuum monochromator (**VAC MC**) is evacuated with a sorption pump. Other symbols are: **L**, MgF_2 lens; **MCP**, microchannel plate detector. Drawing is not to scale.

The limiting resolution based on a monochromator/grating dispersion of 5 Å/mm (cited earlier) and a minimum slit width of 10 μm is 0.05 Å. We verified this value by measuring linewidths for atomic Hg transitions from a discharge lamp that we also use for wavelength calibration. We also confirmed that the linear relations $\Delta\lambda \propto sw$ and $C(\lambda, \Delta\lambda) \propto (sw)^2$ hold down to a 10–15 μm slit width.

The benefit of improved sensitivity and resolution for studying jet-cooled molecules is illustrated by the spectra in Fig. 2. Shown are the observed line shapes for the origin transitions (i.e., vibrationless to vibrationless levels) from the ground electronic state to two Rydberg states of CH_3I. These states have lifetimes of less than 1 ps due to predissociation to a lower-lying dissociative $\tilde{A}$ state.[11] Direct time-resolved measurements are difficult because of the very short lifetimes and the difficult

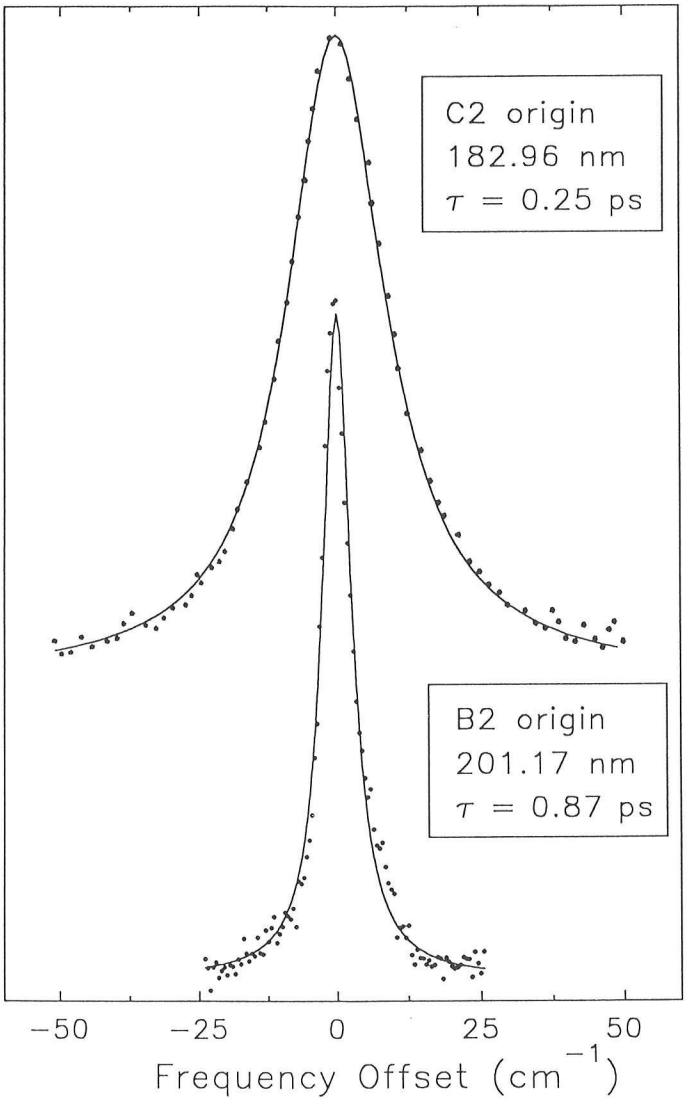

FIG. 2. Direct absorption spectra of the $\tilde{B}$ and $\tilde{C}$ origin transitions of jet-cooled CH_3I. The observed data were fitted to the Lorentzian line shape function $I(\Delta\nu) = [1+ (4\pi\tau\Delta\nu)^2]^{-1}$ where τ is the predissociation lifetime and $\Delta\nu$ is the detuning frequency from line center. Experimental conditions were: $C(\lambda, \Delta\lambda) = 3 \times 10^5$ counts/s at $\lambda = 200$ nm and $\Delta\lambda = 0.008$ nm; $\tau_{gate} = 1$ ms and 50 Hz operation gives a gas pulse duty cycle of 0.05; signal averaging was 4 s/point.

spectral region for laser excitation. Our goal was to measure true lifetime-broadened line shapes by reducing rotational broadening (by supersonic cooling) and instrument broadening to insignificant levels. These spectra were recorded with the use of 15-μm slit widths, which at 200 nm corresponds to a resolving power of $\Delta\lambda/\lambda$ of 1/25,000. By operating at an instrument resolution (2 cm^{-1}) that is much less than the lifetime-broadened linewidth, we could determine lifetimes τ by fitting the observed spectra to a Lorentzian line shape function ($\tau = 1/4\pi\Delta\nu_L$ where $\Delta\nu_L$ is the half-width at half-maximum, Fig. 2).[11] Instrumental conditions for these spectra are given in the caption to Fig. 2.

CONCLUSIONS

We have implemented many of the upgrades suggested in our original account of the UV/VUV supersonic jet absorption spectrometer and achieved an approximately tenfold improvement in sensitivity and a fivefold improvement in sensitivity. There are a few additional upgrades we wish to examine. Foremost is to build a slit nozzle in order to increase the pathlength of the sample. The sensitivity would also improve with the use of a more intense light source. Spectral brightness could be improved by using a pulsed discharge to produce illumination only during the relevant gate periods. An increase in sensitivity could also be achieved by increasing the gas pulse repetition rate, although 100 Hz may be a practical limit. Finally, we have tried using a light guide to achieve better collimation of the light beam in the expansion region; however, losses in light intensity were too great to be useful. A better design may be possible.

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