A Vacuum Ultraviolet, Supersonic Jet Absorption Spectrometer

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A technique for recording high-resolution, broadly tunable absorption spectra in the ultraviolet (UV) and vacuum ultraviolet (VUV) is described. A supersonic expansion is used to prepare molecules in a rovibrationally cold distribution of states, and a dispersed broad-band deuterium (D_2) lamp is used for excitation. The attenuation of light due to absorption is measured with the use of dual gate detection during pulsed valve-on and valve-off periods. The VUV light beam, after crossing the supersonic expansion, is frequency down-converted with a scintillator-coated exit window, and the resulting light intensity is measured by boxcar integration or photon counting. A simple sample delivery system and complete software control of the experiment make this system a routine laboratory spectrometer. Sensitivity and resolution are discussed, and the device is demonstrated for the molecules NH_3 and CH_3I.
Index Headings: **Supersonic expansion; Direct absorption; VUV; Molecular beam.**

INTRODUCTION

The method of supersonic expansion for preparing rovibrationally cold and collision-free molecules is widely employed in high-resolution spectroscopy of polyatomic molecules.[1,2] This procedure considerably reduces the distribution of initial energy states relative to a thermal sample, which in turn accounts for a simplifying reduction in the linewidths and in the number of spectral lines. For thermal samples, resolution is often limited by spectral overlap and congestion, whereas for supersonic expansions, the limiting factor is typically the bandwidth of the light source. Consequently, in the latter case, extremely high resolution is achievable with the use of narrow-linewidth laser excitation. However, laser excitation is not very practical for recording broadly tunable spectra, especially in regions of the vacuum ultraviolet (VUV).

Recent efforts to use high-resolution laser molecular beam spectroscopy as a sensitive and selective molecular detection technique[3–11] have been hampered by the lack of spectroscopic data of sufficient resolution for many large molecules of relevance (i.e., pesticides, nerve agents, polyaromatic hydrocarbons, rocket fuels, biological compounds, etc.). The solution-phase or thermally broadened gas-phase spectra that may exist are usually not of sufficient resolution to assist in searching for efficient and highly selective laser excitation wavelengths for molecular detection applications. Moreover, most laser-based techniques for studying polyatomic molecules rely on laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI) for detecting molecular absorptions. However, the efficiencies of these processes diminish with the lifetime of the absorbing states. For detection of very short-lived states, absorption may become the method of choice.

We report on a direct absorption spectrometer design that benefits from supersonic expansion cooling and offers broad tunability and VUV operation to energies exceeding the ionization potential of most polyatomic molecules. Because the molecular densities in a free-jet expansion are rather low, direct absorption is not a sensitive method of detection, which may explain why relatively few attempts have been made to apply absorption techniques to supersonic expansions. These other efforts have focused on the UV/visible[12–14] or the infrared (IR)[15,16] region of the spectrum, but not the VUV, which we emphasize in this paper. Molecular beam absorption spectroscopy provides a convenient way to obtain high-resolution survey spectra and therefore fulfills an important niche not provided by other available techniques.

EXPERIMENTAL

Pulsed Supersonic Nozzle. The solenoid-driven pulsed valve design has been described before.[17,18] We have since made electronic modifications that allow stable long-term operation at 50 Hz. The following changes were made to our previous circuit:[18] (1) replacement of the Motorola MJ10100 Darlington transistor with a Powerex KS223515, (2) replacement of LED at the emitter of MJ10002 with a series of four IN4004 diodes, and (3) replacement of the 500-Ω resistor at the emitter of 2N2222 with a 180-Ω value. Because of the higher-repetition-rate operation, the valve is cooled by flowing water through ⅛-in. copper tubing wrapped around the solenoid coil. A temperature controller, connected to cartridge heaters and thermocouples embedded in the stainless steel valve body, is used to maintain elevated temperatures when one is using relatively involatile liquid or solid compounds placed in the pulsed valve sample holder. Because a continuous light source is used for excitation (see below), it is advantageous to increase the pulsed valve duty cycle within the constraints of the pumping system (see below). At 50 Hz, we typically operate with a gas pulse width of 600–800 μs, an aperture of 500 μm, and a backing pressure of about 10–25 psi He or Ar. These conditions produce pulsed gas throughputs of about 0.2–1 Torr L/s.

The current pulse valve hardware is actuated with a plastic pin (Kel-F for up to 90°C and Envex for up to 200°C) that seals against a circular orifice. In order to achieve a greater effective pathlength, we have experimented with an endcap that flares out into a slit with a length of 1 cm and a width that matches the orifice diameter of 0.75 mm. The increase in signal by this simple modification was at best 50%. It is expected that a

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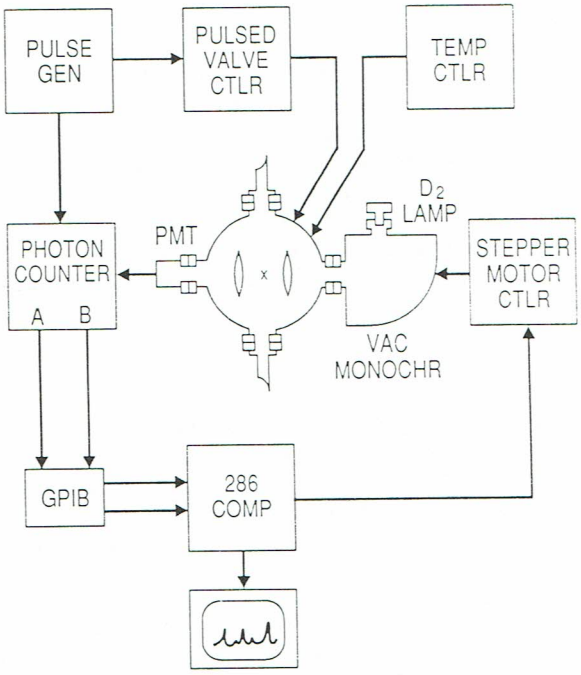

FIG. 1. Diagram of the supersonic jet VUV absorption spectrometer. The pulse valve is at the top of the chamber and the turbomolecular pump at the bottom (neither shown). The × marks the crossing of the molecular jet and the light beam.

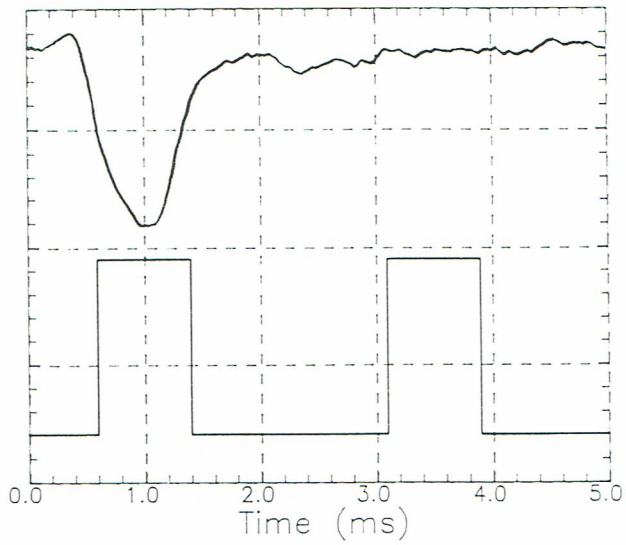

FIG. 2. Oscilloscope traces of the pulsed valve gas pulse (top trace) and the gate intervals used for photon counting (bottom trace). The gas pulse appears as an absorption dip in the analog detected light signal (shown is the average of 1000 pulses). The dip intensity was about 2% of the light intensity for λ = 136.1 nm and an expansion mixture of 20% NH_3 in He at 25 psi. The gate intervals denote the time periods over which photon counting occurs in the actual recording of a spectrum.

true slit nozzle design, based on previous reports,[14,15] could improve the absorption intensity by as much as an order of magnitude.

Vacuum System and Pumping Requirements. An experimental schematic of the molecular beam absorption experiment is given in Fig. 1. Because the number of absorbed photons scales directly with the throughput of the pulsed nozzle, we chose to use a turbomolecular pump for its capability to maintain pumping speed to pressures about an order of magnitude above that of a diffusion pump. The 1500 L/s turbomolecular pump backed by a 16 L/s direct drive mechanical pump maintains an ambient pressure just under 10^{-3} Torr at a foreline pressure of about 100 mTorr when one is using about 15 psi backing pressure of He. A large diffusion pump or roots blower could also support the pulsed valve throughputs used here, although these would have to be baffled to reduce oil contamination that could coat the VUV optics and windows.

Excitation and Detection. A deuterium (D_2) arc discharge lamp (Hamamatsu L-879-01) is used as a broadband UV/VUV light source. The continuous output is dispersed in a 0.2-m Seya-Namioka-type vacuum monochromator (Minuteman VM-302) with a dispersion of 40 Å/mm for a 1200 lines/mm grating. The resolution and light throughput of the monochromatized lamp source scale linearly and to the second power, respectively, with slit width when both slits are set equally. We plan to install a 0.5-m monochromator, which will improve performance significantly. The use of MgF_2 or CaF_2 windows and lenses (transmission cutoff of 119 nm and 128 nm, respectively) defines the short-wavelength limit of the spectrometer. The monochromator is evacuated with a liquid-nitrogen-cooled sorption pump. A 50-mm or 63-mm-focal-length lens of 1 in. diameter is used to focus the slit-shaped output light to a rectangular dimension of about 4 × 2 mm, where the long dimension is parallel to the exit slit and to the direction of the supersonic expansion, which is directed downward into the turbomolecular pump. The light beam crosses the gas and then impinges on a MgF_2 exit window that is coated on the outside with the scintillator sodium salicylate, which absorbs the light and re-emits at wavelengths around 400 nm. This procedure enables one to use a single photomultiplier tube (Hamamatsu R647-04) for measuring the light intensity continuously from the visible to the VUV. A lens is positioned outside of the window and before the photomultipler tube (PMT) to improve the collection efficiency of the non-directional scintillator emission.

Absorption is detected by measuring the difference in light intensity for two gated time intervals, one of which is overlapped with the gas pulse (I) and the other of which is delayed by about 2 ms (I_0) with respect to the gas pulse. This arrangement, illustrated in Fig. 2, approximates a double-beam experiment. The gated signals are measured with either a boxcar integrator/averager (PAR 162/165) or a photon counter (SRS 400). With our current light source, we find that photon counting is preferable because it is immune to PMT dark noise and other analog noise sources that can obscure low absorbance measurements. The use of a more intense light source may exceed statistically reliable photon counting rates (see next section), in which case analog boxcar measurements would be required. A lock-in detector is not considered a good choice due to the low duty cycle (about 4%) for the absorbing pulse-on period.

DETECTION SENSITIVITY

Instrument Noise. The principal sources of noise in a photon-counting experiment are stray light detection, light source fluctuations, and statistical counting noise.

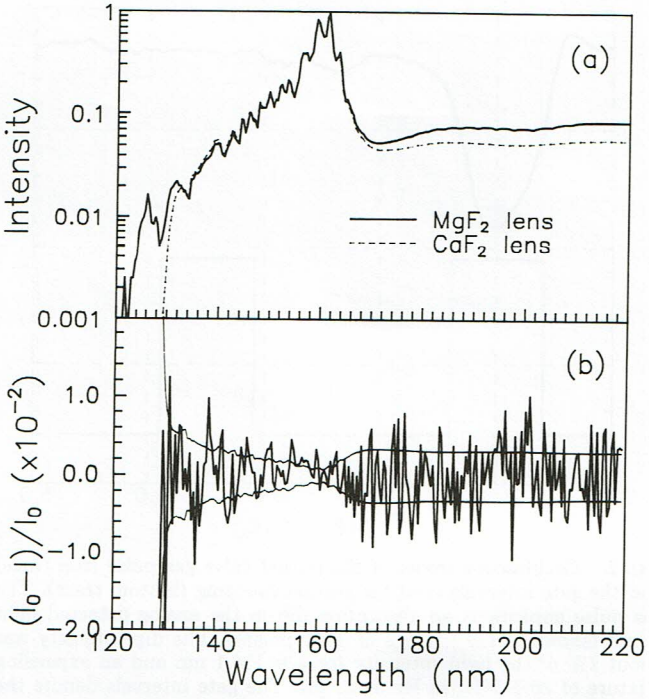

FIG. 3. (**a**) D_2 lamp spectral output and the short-wavelength cutoff for a MgF_2 vs. a CaF_2 focusing lens. (**b**) Observed and calculated (statistical) noise spectrum for the response with the use of a CaF_2 lens. Scanning parameters were: $1/\tau_{rep} = 50$ Hz, $\tau_{gate} = 800$ μs, $n_{pulse} = 200$, and a slit resolution of 0.8 nm.

We begin by considering the latter source, which is due to the statistical fluctuation of counting a finite number of photons emitted randomly from a constant level light source. The root mean square noise fluctuation N_{rms}, expressed as a fraction of the total number of photon counts, is given by

$$N_{rms} = \frac{(C\cdot t)^{1/2}}{C\cdot t} = (C\cdot t)^{-1/2} \tag{1}$$

where C is the count rate and t is the counting time. Clearly, the statistical noise decreases in relative importance with increasing count rate. The maximum count rate, however, is limited by the accuracy of measuring single photon events; an excessive count rate will lead to an unacceptably high probability of pile-up (i.e., two photons arriving at the detector within the instrument temporal resolution). The probability of a double-strike being detected as a single event is a function of the count rate and the pulse-pair resolution of the instrument τ_{res}, and is given by $C\tau_{res}$ in the limit where $C\tau_{res} \ll 1$ and triple-strikes are ignored. The double-strike count rate C_{ds} is then

$$C_{ds} = C^2\tau_{res}. \tag{2}$$

Because C_{ds} is a statistically predictable quantity, it can be treated as a correction factor in the total count rate. This factor would cancel in a double beam experiment where the difference in count rates is measured over two time-gate intervals. However, the noise due to the statistical fluctuation of C_{ds} would persist. It follows from Eq. 1 that the double-strike statistical noise N_{ds} is unimportant relative to N_{rms} as long as $C_{ds} \ll C$ (i.e., when $C\tau_{res} \ll 1$). We attempt to work under conditions where the dispersed lamp output produces a value of $C\tau_{res}$ between 0.01 and 0.10. For a pulse pair resolution of $\tau_{res} =$ 10 ns, this corresponds to count rates of 10^6–10^7 photons/s. As resolution is increased by reducing the monochromator slit widths, the count rates will likewise decrease causing the sensitivity to diminish accordingly.

The fractional noise level $N(\lambda)$ per spectral point λ in an absorption spectrum is governed by the count rate $C(\lambda)$ and the counting duration t according to Eq. 1. The value of t in the pulsed experiment is given by the product of the counting gate width, τ_{gate}, and the number of pulses summed per point, n_{pulses}, according to the expression

$$N(\lambda) = [C(\lambda)\cdot n_{pulses}\cdot\tau_{gate}]^{-1/2}. \tag{3}$$

The dispersed output of the broad-band D_2 lamp is plotted in Fig. 3a for different VUV optics. A dwell time of 4 s per point (i.e., $n_{pulse} = 200$ at a repetition rate of $\tau_{rep}^{-1} = 50$ Hz) was used for this example. The instrument noise spectrum is represented in Fig. 3b and was measured by recording the signal $(I_0 - I)/I_0$ in the absence of sample gas pulses. A comparison of the calculated statistical noise spectrum [Eq. 3] to the observed spectrum indicates that other sources of noise do not contribute significantly to the statistical level. The use of photon counting has effectively eliminated analog noise, and the lamp fluctuations have averaged effectively to zero over the counting period t. The strong resonant output of the lamp at about 160 nm (about a tenfold increase in photon counts) gives rise to a corresponding decrease in the noise level as expected for statistical noise according to Eq. 3.

Sensitivity. The noise level governs the sensitivity of detecting molecular absorptions. Low absorbance signals are described by the relation

$$\frac{(I_0 - I)}{I_0} = e^{-\sigma nl} \sim \sigma nl \tag{4}$$

where $\sigma(\text{cm}^2)$ is the absorption cross section, n(molecules/cm^3) is the molecular density in the excitation volume, and l(cm) is the effective pathlength. An estimate of the minimum detectable value of σ can be made by assuming some typical conditions. The partial pressures behind the nozzle for the molecules of interest commonly range from 5 to 500 Torr. Excitation occurs about 5 mm from the nozzle (about 7 nozzle diameters) at which point the sample has undergone about a 50-fold dilution in density relative to the backing pressure. Assuming an active density of $n = 4 \times 10^{16}$ (about 1 Torr) and a pathlength of $l \sim 0.5$ cm, a 1% absorption would correspond to a cross section of $\sigma \sim 5 \times 10^{-19}$ cm^2. Methods for improving sensitivity are discussed in the Conclusions section.

JET-COOLED VUV ABSORPTION SPECTRA

Examples of VUV jet-cooled absorption spectra are presented in Figs. 4 and 5. The spectrum of NH_3 in Fig. 4 is noted for extensive vibrational progressions in the ν_2 umbrella mode in all of the observed electronic state transitions. This activity is induced by a geometry change from pyramidal in the ground electronic state to planar in the excited electronic states.[19,20] Several excited states are evident; the lowest-lying excited state $\tilde{A}$ is a valence state that undergoes rapid < 1 ps predissociation, which

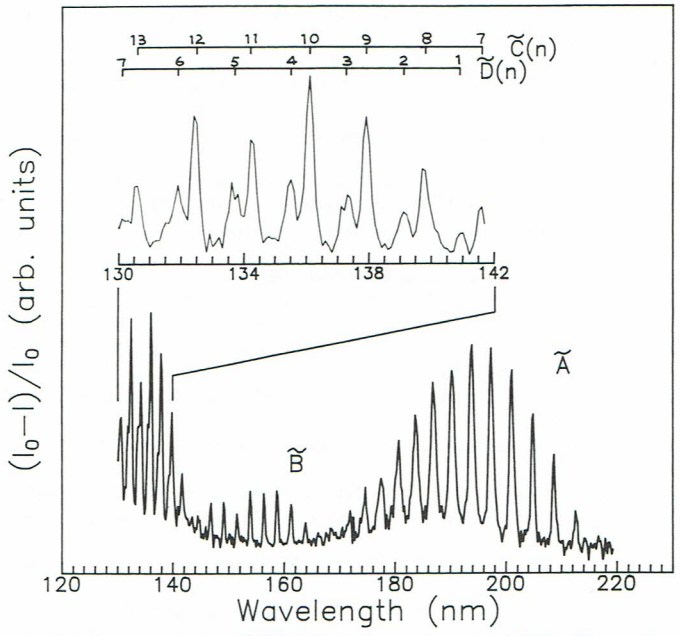

FIG. 4. Supersonic jet VUV absorption spectrum of NH_3. Expansion conditions were neat NH_3 at 12 psi. Scanning parameters for the full spectrum were: $1/\tau_{rep}$ = 50 Hz, τ_{gate} = 800 μs, n_{pulse} = 200, and 0.5-nm slit resolution; and for the expanded spectrum: n_{pulse} = 500 per scan for the sum of 3 scans and 0.2-nm slit resolution.

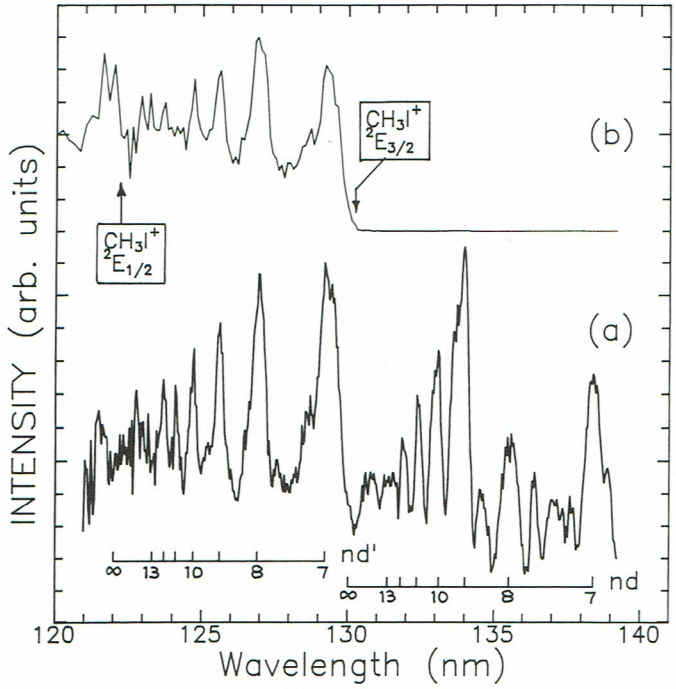

FIG. 5. Supersonic jet VUV spectra of Ch_3I by (**a**) direct absorption (n_{pulse} = 500 per scan for 6 scans and 0.2-nm resolution), and (**b**) ionization (n_{pulse} = 200 per scan for 4 scans and 0.2 nm resolution). The expansion conditions for both spectra were about 25% CH_3I in He at 10 psi. The ionization thresholds for the 3/2 and 1/2 spin-orbit ion-core states are indicated Rydberg series convergences in **a** and by the ion thresholds in **b**.

accounts for the broad linewidths. The higher excited states $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$ are Rydberg states. The Rydberg linewidths are narrower than the $\tilde{A}$ state linewidths due to longer excited state lifetimes. The expanded region shown in Fig. 4 was recorded under high resolution (0.2 nm) to resolve the overlapping $\tilde{C}$ and $\tilde{D}$ state features. Because of supersonic cooling, the spectra in Fig. 4 are free of vibrational hot band structure (i.e., transitions evolving from vibrationally excited levels in the ground electronic state). However, the very narrow rotationally cooled linewidths are not revealed with our current instrument resolution. We discuss in the Conclusions section methods for significantly enhancing sensitivity and resolution. These highly excited states of NH_3 have been extensively studied by multiphoton excitation spectroscopy.[21,22] The purpose of Fig. 4 is to show an example of the first single-photon absorption spectra of these states in a jet-cooled sample.

The VUV jet-cooled absorption spectrum of CH_3I in the vicinity of the ionization potential is presented in Fig. 5a. A pair of very prominent Rydberg series, assigned to *d*-like molecular orbitals,[23] are observed to converge to the ionization potentials associated with the spin-orbit split ion-core states $^2E_{3/2}$ and $^2E_{1/2}$. Parts of other Rydberg series are evident, but are not emphasized here. We also present a single-photon ionization spectrum in Fig. 5b, which was recorded in the same jet-spectrometer with the addition of a microchannel plate detector biased to attract ions formed by VUV excitation. As expected, signal is only detected above the first ionization threshold at 130.2 nm. At higher energies there is a distinct series of discrete absorptions superimposed on the ionization continuum that are readily assignable to the *nd'* Rydberg series by comparison to the direct absorption spectrum in Fig. 5a. This series is associated with the higher-energy ion-core spin-orbit state $^2E_{1/2}$, which has an ionization threshold at 122.0. Yet ionization clearly takes place from these states, indicating that an autoionizing mechanism occurs involving a transition from the 1/2 to 3/2 spin state (i.e., an electron spin flip). This type of autoionization has been observed for rare gas atoms, but is very uncommon in molecules (we know of no other reported examples).[24] This kind of spectroscopic information can be obtained routinely in the VUV jet-spectrometer.

CONCLUSIONS

This report describes a working VUV supersonic-jet absorption spectrometer and demonstrates the feasibility and utility of the approach. The use of gated photon counting achieves the statistical noise limit of detection. We have also presented routine spectra that reveal new spectroscopic details. One of our foremost goals is to improve the spectral resolution; we are currently far from resolving the narrow rotationally cooled linewidths generated by the supersonic expansion. By installing a larger (0.5 m) vacuum monochromator and a 2400 lines/in grating, we expect a fivefold improvement in resolution (to 0.04 nm) without sacrificing photon flux. Operation at higher monochromator grating orders (at the expense of photon flux) can further improve this value. Other modifications are aimed at improving sensitivity. There is a potential for at least an order of magnitude increase in detection by incorporating the following: a multiple pass cell (two mirrors, three passes); a larger-aperture PMT tube and/or solar blind photon counting PMT (the latter to eliminate the need for a scintillator); a light guide for obtaining much better collimation of the dispersed light

exiting the monochromator slit; operation at higher repetition rates (i.e., 100 Hz); and a slit nozzle. A variety of more intense light sources are also under consideration. A pulsed source, for example, could increase brightness by an order of magnitude over the relevant gate periods.

Finally, we mention a number of other spectroscopic techniques based on the VUV jet-spectrometer design. We have already shown the usefulness of measuring single-photon ionization spectra in Fig. 5a for molecular autoionization studies. The addition of a quadrupole mass spectrometer would enable vertical ionization potentials to be measured for molecular cluster species generated in the jet expansion. The shifts in the ionization threshold as a function of cluster size provide valuable information on the incremental binding energies in cluster ions. We have recently succeeded in measuring chemiluminesence from products occurring by predissociation from highly excited electronic states.[25] The dispersed emission spectrum of the product can be analyzed to give the vibrational and rotational distributions, which in turn provide important information on the dissociative mechanism from state-specific excitation in jet-cooled molecules. Perhaps most noteworthy is that these capabilities are available in an instrument that is routine and reliable to operate.

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