Cavity ring down dye laser spectroscopy of jet-cooled metal clusters: Cu_2 and Cu_3

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Direct optical absorption measurements of jet cooled metal clusters formed in a pulsed molecular beam have been made using a sensitive new absorption technique employing pulsed laser sources. Metal clusters and other metal containing species have been observed in this initial study. Absorption measurements of the Cu_3 $^2A'_1$ - $^2E'$ system reveal strong intensities for vibronic bands seen only weakly in previous photoionization and LIF studies due to predissociation of the upper level. A previously unobserved weak band has been identified and tentatively assigned as an excitation out of the higher energy Jahn-Teller component of the cluster ground state. These results illustrate the potential of this approach for studying larger metal cluster species.

1. Introduction

The geometrical structures of metal clusters and the characterization of incipient metallic bonding in these systems have been subjects of great interest in the last decade. Much of the work in this area has recently been reviewed by Weltner and Van Zee [1] and Morse [2]. A number of gas phase metal dimer systems have been spectrally characterized using resonant two photon ionization (R2PI) and laser induced fluorescence (LIF) techniques, but only a few larger clusters have been studied. While trimers, tetramers, etc. are readily produced in supersonic expansions of laser vaporized metal plasmas, rapid internal conversion and predissociation of excited states resulting from the high density of states generally makes these systems inaccessible with either R2PI and LIF.

Conventional absorption spectroscopy would, in principle, be the most general method for probing such species, however the low cluster density in the beam renders such an approach difficult to implement. To address this problem we have utilized a new technique which allows very sensitive absorption measurements to be made on a microsecond time scale over the spectral region accessible with tunable pulsed lasers and non-linear optical conversion [3]. In this paper we present the first results obtained using this technique for the study of gaseous, metal clusters produced in a pulsed molecular beam.

The basis of the optical technique is the measurement of the time rate of absorption of a light pulse by a sample located within a closed optical cavity. As discussed in an earlier paper [3], the absorption measurement is reduced to the determination of the optical cavity decay time, which follows first order exponential form. The approach is then insensitive to large fluctuations in the injection laser amplitude because the determination of the rate of decay is independent of the absolute magnitude of the light pulse. Such fluctuations have presented the greatest obstacle to making sensitive absorption measurements with pulsed laser sources. This new technique thus seems uniquely suitable for the study of laser vaporized metal clusters.

2. Experimental

A schematic representation of the experimental design is shown in Figure 1. The metal cluster molecular beam source is a variation of the type described by Smalley and co-workers [4]. Briefly, the pulsed gas jet is provided by a commercial pulsed valve (General Valve, Series 9) which opens to a backing pressure of 100 - 300 psi of argon gas, purified by passage through a dry ice slurry cold trap. The valve is attached to the gas expansion housing which holds a rotating metal rod. The gas pulse flows around the rod and expands through a small (1 mm diameter, 8 mm long) channel into a large vacuum chamber

evacuated by a Roots pump (Edwards model EH4200). An average chamber pressure of ≈0.2 Torr was maintained with 20 Hz repetition rates.

The output of a KrF laser, which is triggered at approximately the center of the gas pulse (500 μsec long), is focused onto a target metal rod. The metal plasma produced in this vaporization is cooled and transported by the gas pulse and condenses into clusters in the supersonic gas expansion. Using this configuration the typical beam "temperature", as deduced from the rotationally resolved spectra of several diatomic species formed in the beam, is typically ≈30 K. A more detailed discussion of the beam characteristics will be presented in a later paper [5]

The cavity ring down detection system is based on a commercial design (Deacon Research Loss Meter System) which is modified such that the closed optical cavity path overlaps the pulsed molecular beam. The light source is a tunable pulsed dye laser (≈10 nsec width) pumped by a small (1 mJ) nitrogen laser (Laser Photonics) exhibiting a spectral bandwidth of ≈1 cm^{-1}. The optical cavity consists of two dielectric coated mirrors aligned along an axis defined by the output beam of the dye laser. A fraction of the output of the tunable dye laser is coupled, by transmission through one of the cavity mirrors (≈0.01 %), into the cavity, where its amplitude decays with a time constant determined by the sum of the mirror transmission and molecular beam attenuation factors. Weak transmission through the end mirror is directed into a photomultiplier tube. The signal produced at the PMT is proportional to the light transmitted through the mirror, and thus to the light intensity within the cavity. The PMT signal is amplified, digitized, and transferred to a microcomputer which fits the data to a first order exponential decay and calculates the total loss per optical pass through the beam. Narrowband absorption spectra are recorded by scanning the output of a pulsed laser through the selected spectral region containing an electronic transition.
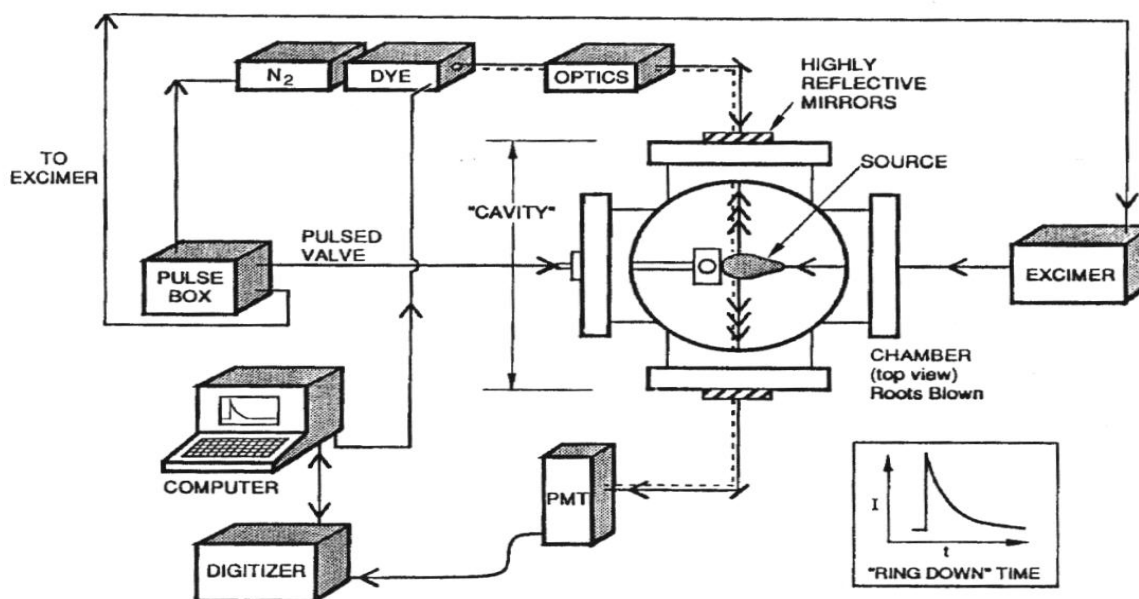

FIG. 1. Schematic diagram of the system used to make pulsed laser absorption measurements of supersonic metal cluster beams. A frequency tunable laser pulse from a dye laser is coupled into the closed optical cavity by transmission through one of the two dielectric mirrors. The light transmitted out of the cell is detected by a phototube, is digitized, and fit to an exponential decay. The spectra are recorded as a rate of loss as a function of wavelength. The pulsed supersonic beam containing the metal clusters intersects the cavity orthogonal to the optical axis. The metal vapor plasma is formed by pulsed excimer laser vaporization of a rotating metal rod mounted in the molecular beam housing.

The mirrors which made up the closed optical cavity were used as vacuum chamber windows and were positioned such that their axis intersected the molecular beam 5 mm in front of the pulsed nozzle orifice. Several different sets of dielectric mirrors were used in these studies. Those which were coated for maximum reflectivity ($\approx$99.99%) in the wavelength range of interest were mounted on soft o-rings seated around a small flange opening, with the coated surface facing into the vacuum. Each mirror was mounted on the chamber and held in optical alignment by adjustable micrometer screws. The total length of the optical cavity (mirror-mirror) was $\approx$55 cm.

Since a mass spectrometer was not available to monitor the composition of the molecular beam, the vaporization conditions were set to parameters consistent with previous studies [4], and were not systematically varied to maximize the production of individual cluster species. The relative timing between laser vaporization pulse and the cavity injection laser pulse was adjusted to provide maximum overlap between the optical cavity decay signal with the transient metal vapor pulse. The behavior of the absorption signal with coarse changes in experimental conditions confirmed that approximate optimization of the conditions was realized.

3. Result and discussion

In this initial application of the cavity ringdown technique for the study of jet cooled metal cluster beams, we chose to study the copper dimer and trimer systems. These molecules have been the subject of several previous investigations by both LIF and R2PI methods; hence, there existed a sufficiently reliable characterization of their spectra and properties to guide these new experiments. Moreover, some interesting questions were left unanswered in the earlier studies that could be resolved by direct absorption measurements.

Initial scans to optimize copper cluster production were carried out on the Cu_2 C-X system [6]. A portion of this system, showing the (1,0) band at 4531.7 Å, is reproduced in Figure 2. The width of the observed transition, $\Delta\omega\approx8cm^{-1}$, is approximately twice that determined by Powers, et al. [6]. This is consistent with our estimate of the cluster beam temperature being $\approx$30 K, as compared to an estimate of $\approx$10 K for the conditions employed by Powers, et al. [6]. The

best signals were obtained with an Ar backing pressure of $\approx$200 psi.

Employing the same operating conditions, a search was initiated for the Cu_3 absorption bands located near 540 nm. This species is interesting because, as a trimer, it is more likely to exhibit excited state predissociation, making detection by R2PI and LIF difficult. In fact, recent studies of this band employing both R2PI and LIF have provided evidence for rapid predissociation [7,8]. A representative spectrum over the range 530 nm $\leq\lambda\leq$542 nm is shown in figure 3. Three strong peaks, at 5398.5, 5356.0, and 5314.4 Å are found, along with several weaker bands. The positions of the strong bands correspond to the bands labeled 2, 5, and 7 in the initial R2PI work on this system [7]. The observed band positions and assignments are presented in Table 1.
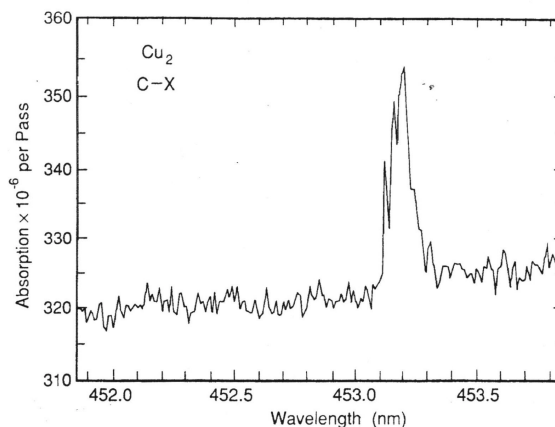

FIG. 2. Cavity ring down absorption spectra of the Cu_2 C-X ($^1\Sigma_g^+$) 1-0 band. The y-axis indicates absorption as the fractional decrease (in parts per million) in the laser beam with each traversal through the cluster sample (half a round trip within the optical cavity). The broad, flat baseline loss rate of $\approx$320 ppm is due to the weak optical transmission through each mirror. The $\approx$8 cm^{-1} bandwidth seen for this band is consistent with a beam temperature of $\approx$30 K.

According to [7], the bands labeled 5,6, 7, and others lying at higher energies (wavelengths shorter than those covered in this work) appear only weakly in R2PI, but are also observed as a depletion in the

density of Cu_3 clusters in the beam following laser excitation. In these experiments, the laser pulse used to populate the various excited vibronic levels of Cu_3 was quickly (≈ 100 nsec.) followed by an ionizing laser pulse having energy sufficient to directly ionize both the dimer and trimer species. The intensity of the trimer ion mass signal was used as a monitor of its concentration in the beam. While a number of additional excited state features were identified using this technique, the resulting band intensities can be distorted due to several effects, including band saturation. Moreover, the shot-to-shot variation in cluster beam density was reported [7] to be a major source of noise, and it is difficult to directly relate the depletion signals to the R2PI intensities.
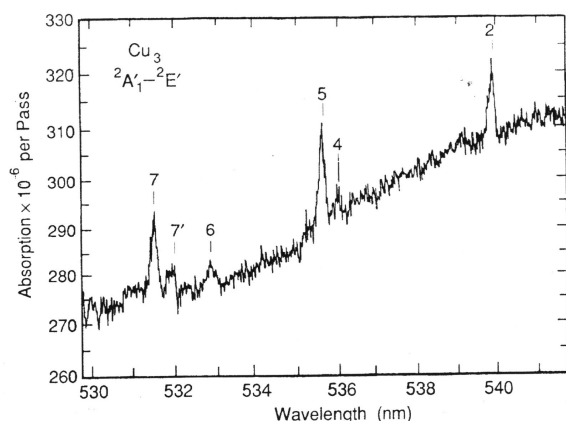

FIG. 3. Cavity ring down absorption spectra of the Cu_3 $^2A'_1$ - $^2E'$ band system near 540 nm. The sloping baseline ranging from ≈ 270 to 310 ppm is due to the variation of the cavity mirror transmission over this wavelength range. The absorption band labels are the same as those used by [7] except for the band labeled 7', which was previously unobserved.

As a result of the upper state predissociation, the intensities of bands 5 and 7 in the R2PI work [7] are significantly lower than that found for band 2; in particular, the intensity of band 7 was only $\approx 3\%$ that of band 2. As is seen in fig. 3, the actual absorption intensities of peaks labeled 2, 5, and 7 are all comparable (with peak 5 being the strongest). Predissociation of the upper states would not be expected to distort the band intensities in absorption as long as the lifetime broadening remained significantly less than the imhomogeneously broadening of the spectra. Examination of the peak bandwidths shown in fig. 3 indicates a fwhm of ≈ 7 cm^{-1} for each of the three bands. While this value is significantly greater than

the ≈ 1.5 cm^{-1} value obtained for band 2 by Morse, et al. [7], it is, again, consistent with the higher estimated beam temperature in the present study (30 K vs. 5 K). We believe that the relative intensities for bands 2, 5, and 7, seen in fig. 3 represent an accurate measure of the relative transition probabilities for excitations out of the vibronic ground state. The availability of such accurate band intensities will aid in understanding the symmetries and geometries of the states involved. While attempts to make these kinds of measurements have been undertaken [9], the results have been difficult to evaluate because of the noted effects of predissociation on the LIF intensities [8].

Table 1
Vibronic band positions and assignments for the Cu_3 $^2A'_1$ - $^2E'$ system seen in absorption

Band number	$\lambda^{a)}$ (Å)	Shift from origin (cm^{-1})	Assignment$^{b)}$
2	5398.5	-	$^2A'_1$ - $^2E'$ origin
4	5360.0	133 cm^{-1}	$1\nu_1$ - A' $^{(c)}$
5	5356.0	147 cm^{-1}	$1\nu_1$ - $^2E'$ origin
6	5328.2	244 cm^{-1}	$1\nu_2$ - $^2E'$ origin
7'	5318.5	279 cm^{-1}	$2\nu_1$ - A' $^{(c)}$
7	5314.4	293 cm^{-1}	$2\nu_1$ - $^2E'$ origin

a) Wavelengths are band centers and are estimated to be +/- 0.5 Å.
b) Upper state designation uses the normal mode nomenclature of ref. [2].
c) A' designates the higher of the ground state Jahn-Teller components, estimated to be ≈ 14 cm^{-1} above the lowest E' level.

A second point of interest involves the band labeled 7' in Figure 3. This band does not appear in the R2PI work [7] due to the weakness of the signal in that region. One possible explanation is that this feature represents a transition out of an excited vibrational level of the ground electronic state. A populated excited vibrational level ($1\omega''$) lying ≈ 99 cm^{-1} above the vibrationless ground state has already been identified in both the R2PI [7] and LIF [8] studies. Assuming that this transition originates in this excited vibrational level, the final state would lie ≈ 377 cm^{-1} above the $^2A'_1$ vibronic ground state. While an excited vibronic level of the $^2A'_1$ is known to exist at this energy (seen as a depletion band and labeled 8 in [7]), we believe this correspondence is fortuitous, and that

an alternative assignment is required for several reasons. If this band were actually due to such a hot band transition, then a second hot band should appear with reasonable intensity at 5384 Å. The upper state of this hot band would be the $1\nu_1$ level (the same as in band 5). The absence of a band at this wavelength (evidently due to a lack of population) in these direct absorption experiments argues against the assignment of the 5318 Å feature as a hot band.

An alternative explanation is suggested by the discussion of the Jahn-Teller effect in the Cu_3 ground state presented by Morse, et al. [7,10]. The degeneracy of the ground state is lifted by Jahn-Teller distortion to produce a pair of $^2E'$ vibronic levels and a $^2A'_1$ level at a slightly higher energy. Excitations out of this $^2A'_1$ level have previously been invoked to assign band 4 [7] (see Table 1). The energy difference between bands 5 and 4 would correspond to this energy splitting in the ground state. This difference, ≈ 14 cm^{-1} from the present data, is exactly the energy defect between bands 7 and 7', lending support to such an assignment. Confirmation of this possibility must await additional studies of the higher energy bands, however.

4. Conclusions

A new spectroscopic technique which allows sensitive direct absorption measurements to be made on pulsed supersonic beams of metal clusters has been described and demonstrated. Absorption spectra have been obtained for the C-X system of Cu_2 and the $^2A'_1$ - $^2E'$band system of the Cu_3 cluster. The band intensities found for the Cu_3 system in the range 5300 - 5420 Å differ significantly from those observed in a previous resonant, two-photon ionization study [7]. The band intensities found in this simple absorption study are not significantly affected by the upper state predissociation and can be used to evaluate the predictions of theories used to model this transition. The new approach, described here, should be applicable to many different cluster species produced in pulsed supersonic expansions.

References

[1] W. Weltner and R.J. van Zee, Ann. Rev. Phys. Chem. 35 (1984) 291

[2] M.D. Morse, Chem. Rev. 86 (1986) 1049

[3] A. O'Keefe, and D.A.G. Deacon, Rev. Sci. Instrum. 59 (1988) 2544

[4] J.B. Hopkins, P.R.R. Langridge-Smith, M.D. Morse, and R. E. Smalley, J.Chem. Phys. 78 (1983) 1627

[5] A. O'Keefe, J.J. Scherer, A.L. Cookly, R. Sheeks, J. Heath, and R.J. Saykally, in preparation

[6] D.E. Powers, S.G. Hansen, M.E. Geusic, A.C. Pulu, J.B. Hopkins, T.G. Dietz, M.A. Duncan, P.R.R. Langridge-Smith, and R.E. Smalley, J. Phys. Chem. 86 (1982) 2556

[7] M.D. Morse, J.B. Hopkins, P.R.R. Langridge-Smith, and R. E. Smalley, J. Chem. Phys. 79 (1983) 5316

8) E.A. Rohlfing and J.J. Valentini, Chem. Phys. Lett. 126 (1986) 113

9) J.W. Zwanziger, R.L. Whetten, and E.R. Grant, J. Phys. Chem. 90 (1986) 3298

10) M.D. Morse, Chem. Phys. Lett. 133 (1987) 8