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Laser induced excitation spectroscopy of copper trimer in various stages of supersonic expansion: Observation of fluorescence from dissociative levels

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Gas phase spectroscopic studies of copper trimer are reported. Using laser induced excitation spectroscopy and a trimer source producing concentrations some three to six orders of magnitude in excess of those available from alternative devices, we obtain the visible spectrum of the trimer. This spectrum has been associated with a ${}^2E''\text{--}{}^2E'$ transition of a D_{3h} molecule in which both electronic states undergo Jahn–Teller distortion. Spectra obtained under a wide variety of experimental conditions encompass the wavelength range 6050–5180 Å corresponding to a range of effective temperatures. Data obtained in the present study are correlated with the recent studies of Morse *et al.* (laser vaporization, R2PI, and depletion spectroscopies) and Moskovits and co-workers (resonance Raman-matrix isolation). The observed spectroscopic features are in one-to-one correspondence with the detailed excited state vibronic calculations of Thompson *et al.* and in some respects may agree with the “first order” ground state vibronic calculations of Moskovits. The generated concentration of trimer molecules is such as to allow the characterization of strongly predissociative levels lost to the R2PI technique. The extent of the observed spectra allow the separation of level structure associated on the one hand with the excited state symmetric stretch mode and on the other with the vibronic levels resulting from the coupling of the asymmetric stretch and bending modes. Significant changes in those features which dominate observed excitation spectra as a function of effective temperature are interpreted in terms of a change in the ground state population distribution and hence an alteration in the configuration space connecting *populated* ground state and accessed excited state levels. These temperature dependent effects and observed hot band structure imply that the pseudorotation barrier in the ground electronic state of the trimer is considerably smaller than previously suggested.

INTRODUCTION

The metal–metal bond and in particular the electronic structure of metal clusters and metallic surfaces has become a topic of intense interest. There has been widespread and growing effort to understand the structures and properties of small metallic clusters.⁵ An increasing number of experimental characterizations are now beginning to balance the impressive array of theories which have been applied to these systems.⁶ Here, we describe an experimental effort and the results of a study which contribute to our understanding of the molecular electronic structure of the copper trimer molecule.

We have been concerned with the development of oven-based high intensity metal cluster sources which allow not only for the production of the requisite clusters but also provide for their formation primarily with low internal temperatures ($T < 300$ K). This requirement is necessary since the analysis of the features which map energy levels, structure, and dynamic behavior may be prohibitive if not impossible at the elevated temperatures required to produce these species through vaporization of the bulk metal. Here, we require a careful mesh of the appropriate material science and the techniques of rarefied gas dynamics to produce an isentropic supersonically expanded “free jet” of cold metal clusters. Once formed, this jet stream of metal clusters can be simultaneously probed using a combination of laser fluorescence techniques and mass spectroscopy.

In this paper, we report a study of the gas phase visible spectrum of the copper trimer molecule which has been associated with a ${}^2E''\text{--}{}^2E'$ transition of a D_{3h} conformation in which both electronic states undergo Jahn–Teller distortion.³ Spectra, taken under a wide variety of experimental conditions, as a whole encompass the wavelength range 6060–5180 Å, corresponding to a diversity of effective temperatures or varying excitation conditions. The observed band system corresponds to an intense transition at ~ 530 nm observed previously and assigned to copper trimer by Moskovits and Hulse⁷ when analyzing the envelope which corresponds to a portion of the absorption spectrum obtained (Cu_n , $n = 1\text{--}4$) after copper is deposited in an argon matrix.

The data obtained in the current study appear to provide some correlation between the recent studies of Cu_3 by Morse *et al.*¹ using R2PI and depletion spectroscopies in conjunction with laser vaporization and the recent resonance laser Raman spectral studies of Moskovits and co-workers.^{2,3} In addition, the observed pattern of energy levels bears a strong correlation with the detailed excited state vibronic calculations of Thompson *et al.*⁴ and a possible correlation with the first order ground state assignments of Moskovits.³ The concentration of copper trimer molecules generated in the present study is such as to allow the characterization of levels which are apparently strongly predissociative and are lost to the R2PI technique. Further, we are able to distinguish and

separate level structure associated on the one hand with the excited state symmetric stretch and on the other with the vibronic levels which result from the coupling of the asymmetric stretch and bending vibrations. Observed hot band structure and the variation of spectral features as a function of temperature allow us to infer that the pseudorotation barrier in the ground electronic state of copper trimer is notably smaller than that implied by Morse *et al.*¹ and may even correspond to an energy increment relative to the zero point energy such that the trimer potential approaches a "Mexican hat" configuration.³

There are several reasons for the present focus on the study of bound-bound transitions in copper clusters. The results obtained for copper can be correlated with recent quantum chemical calculations on the group IB metals.⁸ Indeed, several of these studies have already made contributions to the interpretation of copper trimer features.² Aggregates of copper and silver represent the simplest of the transition metal clusters; in addition they possess reasonable M-M₂ binding energies exceeding 20 kcal/mol.⁸ Matrix isolation spectroscopic studies demonstrate that the dimer, trimer, and tetramer band systems are reasonably well separated.^{7,9} The probable similarity which the copper and silver systems have to the alkali metals has now been demonstrated by Moskovits and co-workers.² It is anticipated that the fluxional nature of alkali clusters and copper trimer should extend to other polyatomic clusters. Thus, it should be well understood in the group IA and IB metals where further spectral complications including significant increases in spin multiplicity (middle transition metal clusters) do not further complicate the treatment of observed spectra.¹⁰

One of the major limitations of matrix isolation spectroscopic studies results from the various homogeneous and inhomogeneous mechanisms which lead to the broadening of guest spectral features reducing detail and accuracy.¹¹ In the limit where no vibrational fine structure is observable, limited spectral information is obtained. Unfortunately, this is the case for the polymeric matrix absorption spectra of the alkalis, copper, and silver, where electronic excitations are to low-lying Rydberg states.¹¹ Therefore, structured emission

and absorption spectra obtained in the gas phase can be used to gain missing insights on internal mode structure and dynamics and hence garner more detailed information on the bonding of small clusters of the group IA and IB metals.

EXPERIMENTAL

We have been concerned with the continuous supersonic expansion of copper vapor, the subsequent formation of the copper trimer molecule in large concentration [$(\text{Cu}_3) > 10^{12}/\text{cc}$], and the characterization of the trimer laser induced excitation spectrum under a variety of experimental conditions. This effort has entailed the development of a versatile high pressure (~ 100 Torr) source which can readily drive the supersonic expansion. In the Appendix we detail the oven design necessary to obtain supersonic high metal mole fraction or pure metal expansions. In the present studies we have made use of a pure metal supersonic expansion where the expansion is complete and the beam is collisionless within 30–50 nozzle diameters of the source.

The oven system described in the Appendix is incorporated in a vacuum system similar to that used in previous studies except that the laser fluorescence detection system and overall chamber pumping systems are configured differently. A schematic outlining these modifications is presented in Fig. 1. Three VHS-6 diffusion pumps evacuated the apparatus to pressures in the range $\sim 5 \times 10^{-7}$ Torr. The two diffusion pumps located away from the oven were pumped with a Kinney KDH-130 mechanical pump while the diffusion pump directly below the oven was rough pumped with a Welch 1397 forepump.

In order to excite fluorescence from copper trimer, an argon ion laser was used to pump one of two cw dye lasers tuned by a homebuilt^{12–14} three stage birefringent filter at a bandwidth of 0.5 cm^{-1} over the range 5200–6600 Å, the portion of operation within this range being dictated by the dyes and optics in use. The output power from the dye lasers ranged between 50 and 300 mW; the laser beam was brought into the apparatus through the Brewster window assembly depicted in Fig. 1. The fluorescence was detected with an RCA IP28 photomultiplier tube. Extensive light baffling

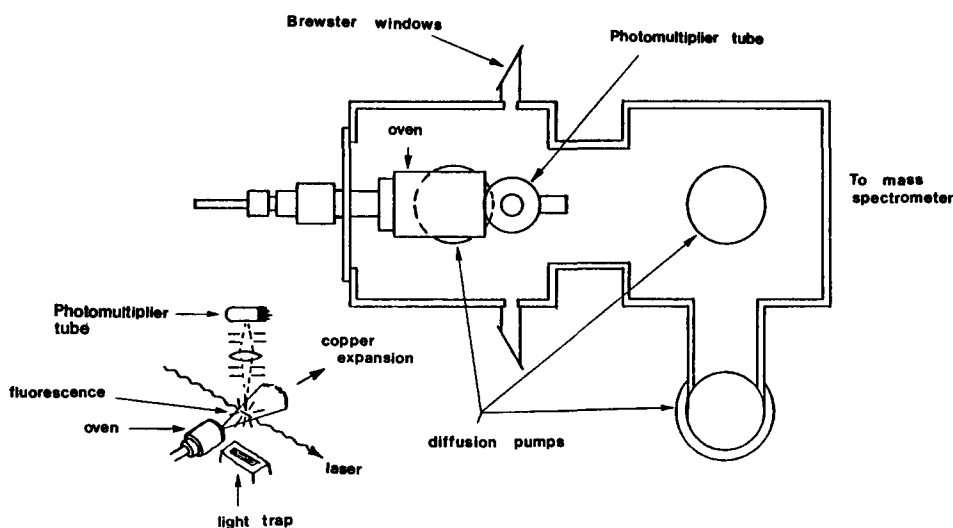


FIG. 1. Vacuum chamber used for copper vapor expansions. See the text for discussion.

(light traps) was necessary to reduce the amount of blackbody radiation reaching the detector. In addition, the output from the dye laser was chopped to allow ac detection of light emanating from the fluorescence viewing zone, ac detection being used to further discriminate between fluorescence and blackbody radiation reaching the detector.^{13,14} The signal was also monitored with an oscilloscope in order to optimize the parameters for observing the fluorescence.

The nozzle sources used in these experiments were capable of producing fluxes of up to 10^{20} molecules/s at the source corresponding to concentrations which approached 10^{12} copper trimer molecules/cc in the laser excitation zone. Under optimum conditions, the fluorescence excited from copper trimer was clearly visible to the eye! The mass spectrometric characterization of the beam constituents can be accomplished in either a dc or ac mode. Detectable ions can be produced using electron impact ionization or photoionization.^{13,14}

In a typical run, a sample of copper shot (Malinkrodt, 99.5%) was vaporized from an appropriate crucible design [exact designs and references to Fig. 8 (Appendix) in following sections]. The sample was slowly heated to its melting point (1356 K). Near this temperature, a substantial quantity of gas was evolved. As soon as this process was completed, the temperature was rapidly increased to a final operating temperature between 2100 and 2800 K. In the present experiments copper trimers were detected using laser induced excitation spectroscopy at a point ~ 4 –6 cm downstream of the nozzle in the configuration described in Fig. 1. The chopped output from the dye laser could be focused to a $200\text{ }\mu$ diam spot at a point intersecting the copper beam but, in general, was passed with only mild focusing through the copper beam, following the path dictated by the Brewster angle windows. The fluorescence was collimated with an f -4 lens located 4 in. from the fluorescence on an axis perpendicular to both the laser and molecular beams. The collimated signal was then focused through a slit and onto a phototube. The last step further reduced the blackbody radiation reaching the detector.

RESULTS

Spectra obtained with varying oven configurations

Laser induced excitation spectra generated for the copper trimer molecule under a variety of conditions bear a close correlation with the elegant R2PI and depletion spectroscopic studies of Morse *et al.*,¹ appear to correlate with the recent laser Raman studies of DiLella *et al.*,² and are in a virtual one-to-one correspondence with the elegant theoretical analysis of Thompson and co-workers.⁴ Further, we find significant changes in the copper trimer excitation spectrum as a function of experimental conditions and hence effective temperatures indicating a complicated ground state potential.

The expansion conditions which we have employed in this study cover a reasonable range of temperature, however, the effective temperature of the copper trimers after supersonic expansion to free flow cannot be determined readily. We can only estimate what limiting rotational temperatures might be reached on the basis of equilibration with the trans-

lational bath. For those conditions of highest pressure (density) drop across the nozzle, the translational temperature distribution should collapse to a value corresponding to 4–10 K. Under the mildest conditions used in this study, the limiting translational temperature is on the order of 50–75 K. In all cases we are expanding from an oven at temperatures between 2000 and 2500 K. Based on recent studies of the antimony dimer¹⁵ and sodium trimer¹⁴ molecules in our laboratory, we anticipate that vibrational cooling will lag rotational cooling to a significant extent and therefore that the effective vibrational temperature may be substantial. This is manifest in the spectra generated in this study. The density of states in copper trimer is substantial and it is not surprising that computer simulations indicate that spectral congestion increases rapidly with temperature leading to an extremely dense spectrum even at $T_{\text{rot}} \approx 100$ K.

In order to compare the present results to those obtained by Morse *et al.*¹ as well as correlate our data with the detailed vibronic calculations of Thompson *et al.*,⁴ we reproduce the spectrum of Morse *et al.*¹ in Fig. 2(a) and present an extended list of the detailed vibronic structure calculated for the E'' vibronic levels of the excited ${}^2E''$ state of Cu_3 in Table I.¹⁶ We have modified the labeling of the experimental spectrum for the sake of this comparison. The larger numbers given in the Fig. 2 correspond to the original numbering of Morse *et al.*,¹ whereas the smaller numerals refer to an assigned numbering based on Table I.⁴ Further hot band spectra are identified with an alphabetic symbol.

Portions of the single photon copper trimer excitation spectrum obtained under the most efficient expansion conditions (cooling) achieved thusfar in our laboratory are depicted in Fig. 2(b). The spectrum was obtained using the crucible design shown in Fig. 8(d) (0.008 in. nozzle—depicted in the Appendix) heated with a thin walled solid radiator. The spectrum was scanned with a Coumarin 535 dye laser stabilized to 50 mW at a bandwidth of 0.5 cm^{-1} . The oven was operated at approximately 2500 K corresponding to a copper vapor pressure of 100 Torr. Based upon the hot band structure observed in the spectrum and computer simulations we estimate $T_{\text{rot}} < 50\text{ K} < T_{\text{vib}}$.

The copper trimer system correlates closely with the 533 nm system observed by Moskovits and Hulse⁵ in rare gas matrices. The observed peaks and peak separations in the lower frequency region of the spectrum correlate well with the spectrum obtained by Morse *et al.*,¹ however, there are several notable additions to the overall spectrum. These additions involve (1) a significant number of ground state hot bands (labeled A, B, C), (2) at higher frequency [bands 4–13, 2_s , 3_s in Fig. 2(b)], the onset of features associated with strongly *predissociating* excited state levels of copper trimer (Morse *et al.*¹ depletion spectrum), and (3) features which taken in combination with the Morse *et al.*¹ and Thompson *et al.*⁴ studies indicate a clear distinction between the excited state symmetric stretch progression ($0_s, \dots, 3_s$) and the E'' (Table I) vibronic levels which result from an appropriate coupling of the bending and asymmetric stretching vibrations of the bent triatomic.

The detailed fit which Thompson *et al.*⁴ have made of the copper trimer excited state E'' vibronic level structure is

TABLE I. Calculated vibronic energy levels of total symmetry E'' for the ${}^2E''$ excited electronic state of copper trimer.^a

State (Thompson <i>et al.</i> ^a)	Energy (cm ⁻¹) ^b (110 basis functions)	(156 basis functions)	Morse <i>et al.</i> (Numbering) ^c
0	0.0	0.0	2
1	146.6	146.6	5
2	244.4	244.4	6
3	292.4	292.4	7
4	376.3	376.3	8
5	430.8	430.8	9(A) ^d
6	440.0	440.0	9(B) ^d
7	511.1	511.1	11
8	571.9	571.9	12
9	585.1	585.1	...
10	640.0	640.0	...
11	648.1	648.1	...
12	711.4	711.3	...
13	731.6	731.6	...
(14)	773.9	773.5	...

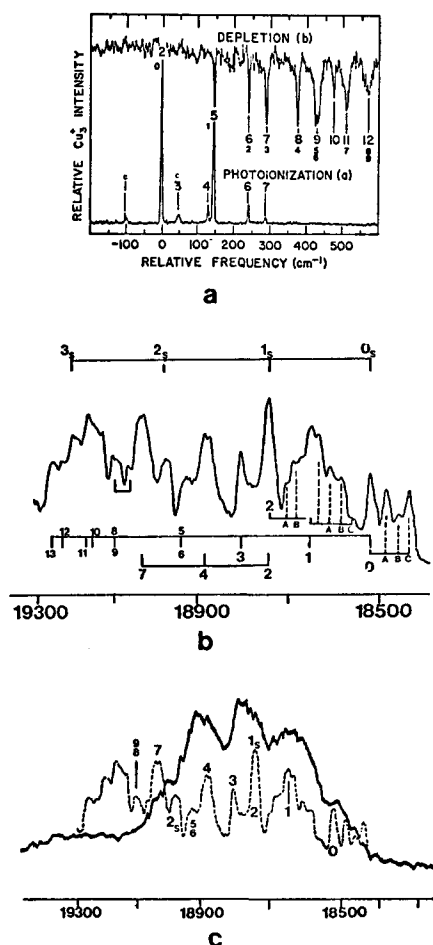
^a Extended from Thompson, Trular, and Mead (Refs. 4 and 16).^b All energy levels relative to zero point of 128.0 cm⁻¹.^c Observed levels of Morse *et al.* (Ref. 1) and present study correspond to those of E'' symmetry. See discussion in Thompson *et al.* (Ref. 4).^d E'' vibronic doublet (see discussion in Ref. 4) partly resolved in study of Morse *et al.* (Ref. 1) but unresolved in present study.

FIG. 2. (a) Copper trimer ion intensity profiles recorded in the photoionization (R2PI) and depletion spectroscopic studies of Morse *et al.* (Ref. 1). The larger numbers indicate the original numbering scheme of Morse *et al.* while the smaller numerals correspond to the numbering scheme from the vibronic calculations of Thompson *et al.* (Ref. 4). Frequency shifts are relative to the origin band at 18 524 cm⁻¹. Letters denote hot bands. (b) Laser induced excitation spectrum for copper trimer in the region 18 400–19 500 cm⁻¹ [coumarin 7 (535)] produced in a "strong" supersonic expansion of the pure metal at a stagnation pressure > 100 Torr. Estimated rotational temperature is $T_{\text{Rot}} < 50 \text{ K} < T_{\text{vib}}$. Vibronic structure is labeled below using the numbering of Thompson *et al.* (Ref. 4). A short progression in the excited state symmetric stretch is labeled above ($1_s, \dots$). Letters denote hot bands. The dye laser cutoffs are at 18 400 and 19 300 cm⁻¹, respectively. The correlation with the R2PI (photoionization) and depletion spectroscopic studies of Morse *et al.* (Ref. 1) is excellent and several additional features are also noted. (c) Cooled laser induced excitation spectrum for copper trimer in the region 18 200–19 500 cm⁻¹ [coumarin 7 (535)] produced in a milder supersonic expansion than the spectrum (b). The effects of heating lead to a merging of the features in (b) and the burning out of higher frequency spectral features. The estimated rotational temperature is $T_{\text{Rot}} \sim 100 \text{ K}$. The 145 cm⁻¹ frequency separations corresponding to vibronic features 0(2), 1(5), 3(7), and 5,6(9) in (a) and (b) are still apparent in the figure. The dye laser cutoffs are at 18 200 [Fig. 3(a)] and 19 300 cm⁻¹, respectively.

impressive. Not only do their calculations simulate the level structure observed in R2PI and depletion spectroscopy,¹ but also there is a one-to-one correspondence between the additional vibronic excited state levels which we observe at frequencies higher than 19 000 cm⁻¹ and their predicted level structure. There are, however, two features indicated in the spectrum [Fig. 2(b)] which these authors do not calculate.

The first of these, lying between the (5 + 6) and (7) vibronic features, corresponds to the feature (10) in the depletion spectrum of Morse *et al.*¹ It is marked from above with a 2_s label in the current excitation spectrum. This band is shifted from the origin (0_s) by $\sim 476 \text{ cm}^{-1}$ and has been assigned by Thompson *et al.*⁴ to the fundamental of the excited state symmetric stretch. A second feature (3_s) in the Cu_3 excitation spectrum lies between the (10 + 11) and (12 + 13) vibronic features and is shifted by $\sim 700 \text{ cm}^{-1}$ from the origin (0_s). The separations of these two peaks, 224 cm⁻¹, and the apparent anomalously large intensity associated with the feature labeled 2–1_s in the observed excitation spectrum cause us to conclude that the feature assigned by Thompson *et al.*⁴ to the fundamental symmetric stretch frequency corresponds, in fact, to two quanta of the symmetric stretch (see also the following). We conclude that the symmetric stretch fundamental (1_s) is virtually isoergic with a trimer vibronic band, the overlap of these two bands producing the more intense feature shifted from the origin band by $\sim 245 \text{ cm}^{-1}$. We believe that this is the frequency of the excited state symmetric stretch fundamental.

The features assigned to hot bands in Fig. 2(b) are shifted by $45 \pm 5 \text{ (A)}$, $80 \pm 5 \text{ (B)}$, and $100 \pm 5 \text{ cm}^{-1} \text{ (C)}$ from the origin band (0_s) and from certain E'' vibronic features [1 and 2 in Fig. 2(b)] associated with the trimer excited state. Note that the hot band structure appears to be readily associated with only the lowest vibronic levels.

We find that the trimer excitation spectrum undergoes significant changes as a function of experimental conditions, the most profound effects resulting from what would appear to be a change in effective temperature and, as a result, the distribution of populated levels. As the efficiency of the expansion decreases or the expansion intersects a component

of background gas,¹⁴ we observe [Fig. 2(c)] the merging of features in the lower frequency portion of the spectrum [vs Fig. 2(b)] and, at frequencies corresponding to higher excited state energies, the "burning out" of several spectral features (vibronic bands 8–13, symmetric stretch level 3_s). While the finer details of the vibronic structure (dashed line spectrum) are now absent, a group of five features separated by the 145 cm^{-1} vibronic frequency separation [see also Fig. 3(a) and Table I] are clearly apparent.

The spectrum depicted in Fig. 3(a) was obtained using the inner oven design diagramed in Fig. 8(c) of the Appendix. Here, the crucible is not heated using the "open" slotted or solid radiator but rather the copper is vaporized from a much tighter configuration; the radiator–crucible design confines the copper with a tungsten crucible incorporating a "press fit" high density graphite nozzle ($d = 0.010\text{ in.}$). The crucible is held in place by a two piece radiator made of CS grade graphite. In order to produce the spectrum depicted in Fig. 3(a), current was passed through the outer radiator sheath to obtain a temperature between 2200 and 2300 K (Cu vapor pressure ~ 10 –20 Torr). The spectrum was scanned with a coumarin 535 dye laser stabilized to 90 mW at 0.5 cm^{-1} bandwidth. Based on a comparison with several previous studies,^{14,15} we estimate $T_{\text{Rot}} < 100\text{ K} < T_{\text{Vib}}$.

With a further increase in effective heating, Figs. 3(a) and 3(b), taken in tandem, demonstrate that the trimer spectrum in the $18\,500$ – $19\,300\text{ cm}^{-1}$ range again changes. The spectra were taken using different oven configurations, the latter of which leads to further heating of the expansion, but very similar dye laser scanning parameters. The dominance of the $\sim 145\text{ cm}^{-1}$ frequency separations in Fig. 3(a) is lost in Fig. 3(b) and the dominant frequency separation now appears to correspond to $\sim 245\text{ cm}^{-1}$. The lower scan in Fig. 3(b) was taken at a lower effective temperature than was the upper trace depicted in the figure. The dye laser used to obtain the lower scan cut off at $18\,500\text{ cm}^{-1}$, whereas that for the upper scan extended to $18\,450\text{ cm}^{-1}$. We suggest that the apparent observed frequency separations in Fig. 3(b) are not dominated by excited state vibronic structure but rather by a progression in the upper state symmetric stretch frequency.

The spectra in Fig. 3(b) were obtained with the radiator–crucible design depicted in Fig. 8(e) of the Appendix. The radiator was operated at a temperature between ~ 2100 – 2250 K corresponding to a copper vapor pressure between 5 and 25 Torr. We estimate that the rotational temperature associated with the spectrum depicted in Fig. 3(b) exceeds 100 K but is not more than 200 K.

Hot band spectra

We have generated an additional catalog of copper trimer hot band spectroscopy. If conditions are changed so as to provide considerable additional heating to the expanding trimers, the red shifted spectrum depicted in Fig. 4(a) can be obtained as a limiting case. The trimer molecules giving rise to this spectrum were produced through direct heating of the crucible depicted in Fig. 8(a) of the Appendix; no radiator was used, current passing directly through the crucible. A rhodamine 6G dye laser with a stabilized output power of 300 mW and bandwidth of 0.5 cm^{-1} was used to excite the spectrum over the range $16\,500$ – $17\,800\text{ cm}^{-1}$. This hot band spectrum is considerably weaker than those spectra generated in the frequency range $18\,500$ – $19\,300\text{ cm}^{-1}$ (Figs. 2 and 3). While the crucible temperature was maintained at 2000 – 2100 K corresponding to an upper bound vapor pressure of ~ 5 Torr and the vapor escaped through a nozzle of diameter 0.008 in. , small amounts of copper could be found vapor deposited on the internal oven parts indicating some pressure loss from the crucible which must lead to a decrease in the cooling effect of an already mild expansion. It should be apparent that an effective vibrational temperature giving rise to the spectrum in Fig. 4(a) considerably exceeds that for those spectra depicted in Figs. 2 and 3. However, the effective rotational temperature may not be comparable and, in fact, may considerably lag the vibrational temperature.¹⁷

As Fig. 4(a) demonstrates, the hot band spectrum is dominated by 145 and $\sim 240\text{ cm}^{-1}$ frequency separations, the former characteristic of a vibronic frequency separation in the $^2E'$ excited electronic state and the latter possibly associated with the excited state symmetric stretch. We also observe frequency separations which might possibly be associated with a short progression in what has been assigned as

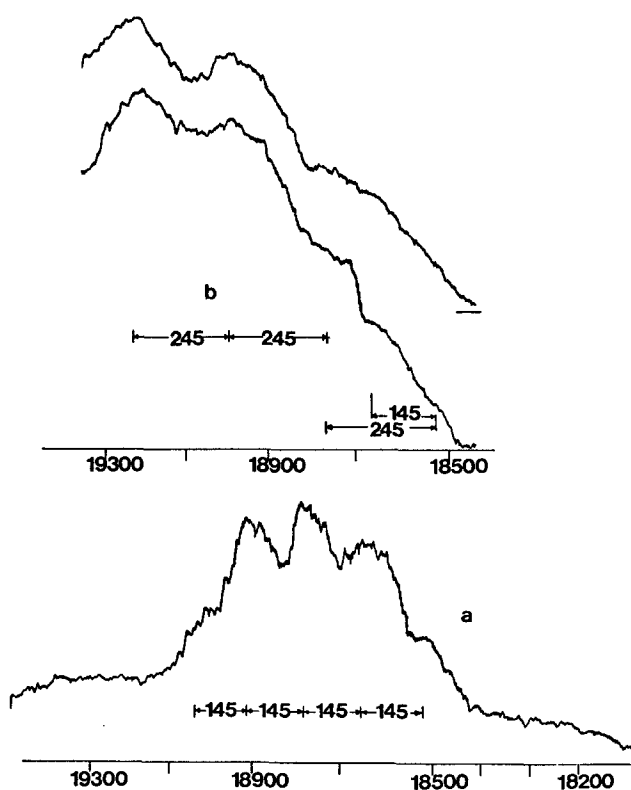


FIG. 3. Laser induced excitation spectra obtained in progressively milder stages of supersonic expansion showing a change of those excited state features dominating the spectrum. (a) Laser induced excitation spectrum in the region $18\,400$ – $19\,400\text{ cm}^{-1}$ dominated by 145 cm^{-1} peak separations corresponding to excited state vibronic structure ($T_{\text{Rot}} \sim 100\text{ K} < T_{\text{Vib}}$). (b) At higher effective temperature ($100\text{ K} < T_{\text{Rot}} < 200\text{ K}$) the dominant spectral features in the region $18\,500$ – $19\,400\text{ cm}^{-1}$ correspond to peak separations ($\sim 245\text{ cm}^{-1}$) indicative of the dominance of the trimer excited state symmetric stretch.

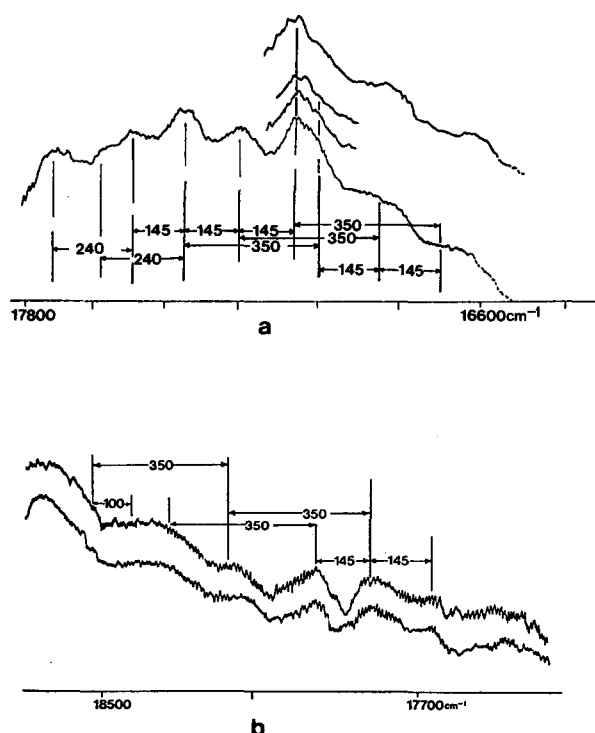


FIG. 4. (a) Copper trimer excitation spectrum in the region 16 500–17 800 cm^{-1} (rhodamine 6G) produced in mild supersonic expansion showing the results of pumping from a vibrationally “hot” and rotationally “warm” ground electronic state. Observed band separations appear dominated by $a \sim 145 \text{ cm}^{-1}$ excited state vibronic separation. In addition, $\sim 245 \text{ cm}^{-1}$ separations and possibly $\sim 350 \text{ cm}^{-1}$ separations which may correspond, respectively, to excited and ground state symmetric stretch frequencies may also be present in the spectra. (b) Copper trimer excitation spectrum in the region 17 600–18 550 cm^{-1} (rhodamine 110) produced in mild supersonic expansion and showing the results of pumping from a vibrationally hot and rotationally warm ground electronic state. The spectrum in this region may indicate some 145 cm^{-1} vibronic separations although they are not dominant. Features shifted ~ 350 and $\sim 700 \text{ cm}^{-1}$ to the red of the origin band can be identified, however, any low frequency modes shifted by less than 100 cm^{-1} from the origin ($18\,524 \text{ cm}^{-1}$) are completely merged.

the Cu_3 ground state symmetric stretch frequency ($\sim 350 \text{ cm}^{-1}$) by DiLella *et al.*, however, this is only a tentative association.²

Some additional credence to the possible observation of overtone spectra corresponding to the assigned² $\sim 350 \text{ cm}^{-1}$ Cu_3 “symmetric stretch” frequencies comes from the hot band spectra in Fig. 4(b) obtained over the range 17 600–18 550 cm^{-1} . Again this hot band spectrum is notably weaker than the spectra generated in the frequency range 18 500–19 300 cm^{-1} as can be evidenced by the rise in intensity at the end of the dye laser profile. The trimer molecules giving rise to the spectra were produced from the directly heated crucible depicted in Fig. 8(b) of the Appendix. A rhodamine 110 dye laser with stabilized output powers of 70 and 80 mW was used to excite the observed bands. Again, we discern what appears to be the 145 cm^{-1} vibronic separation although the features are not as pronounced as those associated with the limiting spectrum [Fig. 4(a)]. This may be a manifestation of the lower laser powers obtained in this region, however, it might also be associated with a very different character for those two distinct regions of the potential

from which we are pumping. Also apparent in the spectrum are features which may be associated with the assigned Cu_3 ground state symmetric stretch frequency. There are clear features shifted ~ 350 and $\sim 700 \text{ cm}^{-1}$ to the red of the Cu_3 origin band at $18\,524 \text{ cm}^{-1}$. Note also that low frequency modes shifted by less than 100 cm^{-1} from the origin are completely merged in the hot trimer spectrum. We have only indicated the region over which we might expect them to appear. Regardless of the relative R6G and R110 pump powers used to obtain the spectra in Figs. 4(a) and 4(b), it is clear that the behavior of the trimer molecule as manifest by the excitation of apparently different vibronic and symmetric stretch combinations reflects the excitation of two distinctly different potential regions.^{17,18}

A further point of interest arises upon comparing the intensity patterns for the laser induced excitation spectrum [Fig. 2(b)] and the R2PI (photoionization) spectrum [Fig. 2(a)]. On the basis of their intensity distribution and that of the origin band relative to other features in the spectrum, Morse *et al.*¹ reason that the states of copper trimer involved in the $^2E'' \rightarrow ^2E'$ transition are quite similar. The laser induced excitation spectrum, although taken across a spectral region in which the phototube response rises with increasing frequency, seems to indicate that the two states may in fact be very different. This is also confirmed by the recent studies of Rohlfing and Valentini¹⁹ who have recently obtained an extensive fluorescence spectrum after pumping ultracold copper trimers to the origin and first excited vibronic level of the $^2E''$ excited state of the trimer. A comparison of the R2PI and depletion spectra of Morse *et al.*¹ demonstrates that only the excitation of the origin band of the transition is free of significant predissociation. In a two-photon experiment one can certainly prejudice the intensity of predissociating levels relative to those which are not predissociative. In fact, the relative intensities of the origin band and the first excited state vibronic level are not drastically different even though this first level undergoes considerable predissociation. We feel that the argument favoring a transition between two quite different states is compelling.

DISCUSSION

Correlations with previous studies and potential extensions

We have observed extensive spectra which correspond to what is believed to be a $^2E'' \rightarrow ^2E'$ transition in the copper trimer molecule.^{1,4} The peak separations which characterize the spectra under a variety of experimental conditions not only correlate well with the recent observations of Morse *et al.*¹ but also with the detailed excited state vibronic calculations of Thompson *et al.*⁴ They also appear to bear some correlation with the observations of Moskovits *et al.*^{2,3}

Those features indicated in the depletion spectrum of Morse *et al.*¹ correspond to strongly predissociating levels. Therefore, using the continuous source outlined in the present discussion, we observe excitation spectra from several levels which are lost to the two-photon resonant photoionization technique. Based on this result and a comparison of the relative sensitivities of the single photon laser induced excitation and resonant two-photon ionization techniques, it

is apparent that our source of copper trimer produces a concentration between three and six orders of magnitude greater than others currently available. Using the present source with its significant range, the extension of the present studies to characterize the ground and excited state of small clusters of the transition metal elements represents a logical future step. One possibility, which correlates well with recent studies of sodium trimer photodissociation to both excited ($\text{Na } ^2P$) and ground state sodium^{14,20} atoms, involves the characterization of nickel trimers or iron dimers and trimers, all of which appear to be inaccessible using a combination of laser vaporization techniques and resonant two-photon ionization spectroscopy.²¹ In other words, given the high density (intensity) obtained with the present source, it may be possible to overcome those loss mechanisms [intramolecular energy redistribution, strong predissociation, and in some cases photodissociation (reflection spectroscopy)] which blind resonance ionization detection techniques. We would be remiss if we did not mention the correlation of our observation of fluorescence from strongly predissociating levels and the observations of Imre *et al.*²³ in their elegant study of the dynamics and resonance Raman spectra of dissociating excited states.

Pseudorotation barrier in the ground state of copper trimer

The changes which are manifest in the copper trimer excitation spectrum as a function of varying experimental conditions are intriguing, and we believe can be used to cast some light on the nature of the trimer ground state potential. This is significant for the nature of the ground electronic state of the trimer is currently the subject of some controversy. Both Morse *et al.*¹ and Moskovits *et al.*^{2,3} have obtained data which indicates that Cu_3 undergoes a Jahn–Teller distortion, however, Morse *et al.*¹ interpret their “hot band” data as indicating a strongly coupled Jahn–Teller surface with a substantial barrier to pseudorotation. In contrast, Moskovits³ interprets the data obtained in his laboratory as resulting from a potential surface almost without barrier to pseudorotation.

The correlation of the current data obtained through excitation spectroscopy with the elegant spectroscopic studies of Morse *et al.*¹ has provided an important link in the identification of the copper trimer spectrum. However, while the impressive study of Morse *et al.* provides a base on which to build, the current data associated with the variation of monitored spectral features with effective temperature and with the observation of hot bands for the ground electronic $^2E'$ state, correlating with excited vibronic and symmetric stretch frequencies, would seem to indicate an interpretation closer to that given by Moskovits.³

Cu_3 represents an example of a class of molecules thought not to have a definite shape in their ground states.²³ The Cu_3 molecule, if it adopts an equilateral triangle configuration (D_{3h}), corresponds to a $^2E'$ ground electronic state which will distort according to the Jahn–Teller theorem along a coordinate which belongs to the direct product representation $E \times e$. The ground state potential surface which represents the nature of this behavior is usually plotted (Fig.

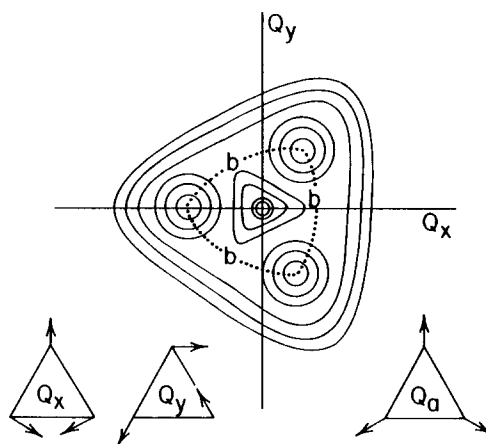


FIG. 5. Contour map of the potential energy surface of a triatomic molecule, X_3 , capable of exhibiting the dynamic Jahn–Teller effect. Taken in part from Ref. 3.

5) as a contour map in Q_x , Q_y space, where Q_x and Q_y represent normal coordinates describing the e' vibration of an X_3 molecule.²³ These coordinates would correlate with a bending and asymmetric stretching vibration if the molecule were reduced to C_{2v} symmetry. The surface consists of three minima which correspond to equivalent “obtuse” forms ($> 60^\circ$) of the X_3 molecule separated by three barriers representing saddle points at the top of which the molecule has an “acute” form ($< 60^\circ$). The obtuse and acute configurations are defined with respect to the $60^\circ D_{3h}$ configuration. At the D_{3h} geometry, the surface displays a maximum, higher in energy than the barriers between the obtuse minima.

The surface described above and in Fig. 5³ is classified in terms of two parameters.²³ The Jahn–Teller stabilization energy is defined as the difference in energy between the D_{3h} form and the minimum energy obtuse angled configuration. The barrier to pseudorotation, which corresponds to the height of the acute angled saddle point above the obtuse angled minimum, is of fundamental importance in determining the dynamics of the copper trimer molecule. When the barrier is high, the molecule will be localized in one of the three obtuse angled minima and the observed energy level pattern should correspond to that of an ordinary bent triatomic. When the barrier is low, the molecule can easily translate from one minimum to another, does not adopt a definite shape, and is able to access a much wider region of configuration space.

In interpreting the copper trimer spectrum for both the ground $^2E'$ and excited $^2E''$ electronic states it is imperative that one establish the Jahn–Teller stabilization and pseudorotation barrier. Morse *et al.*¹ first suggested that the upper $^2E''$ state of the observed Cu_3 transition was weakly Jahn–Teller coupled. Thompson *et al.*⁴ have carried out their analysis within the weak Jahn–Teller coupling approximation to obtain what appears to be a definitive assignment of the excited state vibronic structure to which we have compared previously. In contrast, the parameterization of the ground state is controversial. Morse *et al.*¹ compute a ground state Jahn–Teller stabilization energy of 543 cm^{-1} and a barrier to pseudorotation of 407 cm^{-1} . On this basis, these authors

predict that a 2A_1 vibronic level thought to be observed experimentally at an energy of 15 cm^{-1} is only 2.8 cm^{-1} above the lowest ground vibronic level. Moskovits³ suggests that copper trimer in its ground state is *dynamical* Jahn–Teller molecule and that the barrier height is close to zero where the potential surface would adopt the shape of a Mexican hat consisting of a high central cone surrounded by a moat which rises to form a cylindrical brim (Fig. 5).²³ This interpretation is also consistent with recent calculations of the Cu_3 ground state surface by Miyoshi *et al.*²⁵ and Richtsmeier *et al.*²⁶ who find that the acute and obtuse forms of Cu_3 are approximately isoenergetic. This implies a very low barrier, in contrast with, for example, Na_3 for which the obtuse and acute forms differ in energy by more than 200 cm^{-1} .²⁶

Using the closed form expression for the Mexican hat potential, Moskovits obtains an acceptable fit to the vibronic fine structure of his resonance Raman spectrum. In this limit, Moskovits predicts that the three lowest E' vibronic states lie 50 , 100 , and 124 cm^{-1} above the ground vibronic state leading to hot bands at -50 , -100 , and -124 cm^{-1} due to transitions of the form $E'(n,j) \rightarrow E''(0,1/2)$.²⁷

We believe that the copper trimer excitation spectra generated in our laboratory indicate (1) that the pseudorotation barrier is considerably smaller than that suggested by Morse *et al.*¹ and (2) that the negligible pseudorotation barrier suggested by Moskovits³ may represent a reasonable first order description of the copper trimer ground state. The three hot bands labeled A, B, and C in Fig. 2(b) might be associated with the anticipated location of hot bands representing those levels correlating in the limit with the $E'(n,j) \rightarrow E''(0,1/2)$ transitions²⁷ when the *pseudorotation barrier is low but not negligible*. An alternative assignment, however, consistent with the fluorescence data obtained by Rohlfing and Valentini¹⁹ who observe a set of three closely spaced ground state vibronic levels symmetric about 230 cm^{-1} , suggests that the 80 cm^{-1} feature corresponds to an unresolved combination of these ground state vibronic levels ($\sim 230\text{ cm}^{-1}$) and the first excited state vibronic level at 145 cm^{-1} (red shift from origin $\sim 85\text{ cm}^{-1}$). Further hot band transitions involving a combination of the vibronic and symmetric stretch potentials might also explain at least the 50 cm^{-1} and possibly the 100 cm^{-1} red shifted features.

Of possibly more significance, a low barrier to pseudorotation may also explain the characteristic changes in the copper trimer excitation spectrum as a function of varying expansion source and increasing effective temperature. Specifically we consider the changes associated with the spectra in Figs. 3(a) and 3(b) where the cooler spectrum in Fig. 3(a) is dominated by a 145 cm^{-1} vibronic progression and the spectra in Fig. 3(b) are apparently dominated by the Cu_3 excited state symmetric stretch. A small barrier to pseudorotation may lead to profound temperature dependent effects in the observed emission spectra for a fluxional triatomic molecule. The behavior of the molecule may alter with increasing temperature as those levels lying above the pseudorotation barrier but within the Jahn–Teller well are given to an increasingly higher molecular population. We suggest that this variation in the population distribution with temperature can lead to an effective variation of the configura-

tion space available to the molecule as a function of temperature such that the dominant spectral features associated with the transition are altered.

The nature of populated vibrational–rotational levels, “Franck–Condon” factors,²⁸ and the configuration space associated with transitions involving the copper trimer symmetric stretch potential are not expected to vary greatly with temperature.³⁰

In contrast, although the vibronic states are characterized by good wave functions for which Franck–Condon factors may be calculated in a straightforward fashion, the form of the vibronic wave functions and the configuration space available to the copper trimer molecules varies considerably above and below the pseudorotation barrier; the nature of optical pumping from vibronic levels below and above the pseudorotation barrier is expected to be quite different. We suggest that the rovibronic levels accessible to optical pumping are spread over a much wider range of the ground and excited state as temperature and the density of available states above the pseudorotation barrier increases. When the trimer molecule translates from one region which would correspond to an obtuse configuration to another, refusing to adopt a definite shape, this promotes a spreading over a wider region of configuration space. Although the configuration space²⁸ associated with the pumped vibronic configurations is expanded, the effect on the symmetric stretch level structure is negligible. As a result, the spectrum [Fig. 4(b)] is eventually dominated by the “less diluted” symmetric stretch progression.

Excited state symmetric stretch

The detailed and elegant vibronic analysis of the copper trimer excited electronic ${}^2E''$ state by Thompson *et al.*⁴ plays an important role in the identification of features associated with the cold copper trimer excitation spectrum. A consequence of the present analysis, however, indicates that the excited state symmetric stretch fundamental suggested by Thompson *et al.*,⁴ $\omega_s = 476\text{ cm}^{-1}$ must be revised. We assign the group of four features indicated as 0_s , 1_s , 2_s , and 3_s in Fig. 2(b) as a progression in the trimer excited state symmetric stretch frequency inferring $\omega_s = 255 \pm 5\text{ cm}^{-1}$, $\chi_s = -8 \pm 2\text{ cm}^{-1}$.

Extensions of the present study

Although we have obtained additional information concerning the behavior of the copper trimer molecule, much work remains to be done. Included in this effort must be an attempt to use our intense copper trimer source to generate a high resolution excitation spectrum by scanning the 5397 Å ($18\,524\text{ cm}^{-1}$) origin band. Further questions are raised by the distinctly different structure associated with the trimer excitation spectrum in various frequency regions especially encompassing the hot band spectra in Figs. 4(a) and 4(b). In the near future we hope to cast some additional light on this region using a high metal mole fraction seeded copper (in argon or helium) expansion in order to promote a more pronounced rotational cooling while maintaining the vibrational excitation apparent in the hot band spectra of Figs.

4(a) and 4(b).¹⁵ In other words, we will attempt to obtain rotationally cooled hot band spectra.

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APPENDIX

A supersonic expansion source for refractory metals can be formulated at two extremes using either a pure metal expansion (driven only by the vapor pressure of the metal) or a seeded expansion where a high pressure carrier gas entrains a low pressure metal vapor on its route through a supersonic nozzle. We have focused primarily on seeded expansions of high metal mole fraction or pure metal expansions. At 2300 K, molten copper attains a vapor pressure of ~ 30 Torr, more than sufficient to drive a supersonic expansion into a vacuum of 10^{-5} Torr provided that the vapor can be confined adequately at these temperatures. This figure represents a lower bound to the pressure range over which we choose to operate. The accomplished upper bound design target corresponds to a source which sustains a temperature of 2800 K for a period of operation up to 4 h (charge typically 0.25–0.35 g mol metal). In this appendix we outline the experimental design used to attain these conditions for a pure or seeded high metal mole fraction copper expansion.

Figures 6 and 7 correspond to two cross sectional views of the high temperature oven system used as the copper trimer beam source, the latter schematic including an exemplary radiator plus crucible combination and demonstrating also the installation of the tungsten inlet for seeded gas oper-

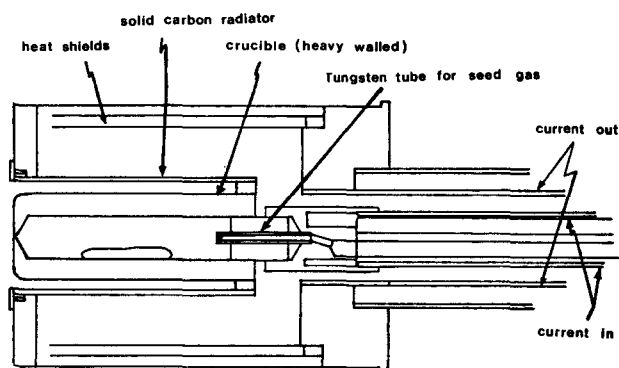


FIG. 7. Copper oven, assembled cross section along center line.

ation. The plane of the cross section in Figs. 6 and 7 passes through the center line of the cylindrically symmetric oven. This oven system which has been operated with a crucible plus radiator combination or by passing current directly through the crucible, is designed for the nozzle vaporization of metals at temperatures up to 2800 K, although it has been operated at substantially higher temperature. The conducting path of the oven is similar to a coaxial cable with its central wire connected to the outer ground sheath. Current travels through the center of the oven and then out along the outer walls. The use of concentric copper pipes provides a large conductor cross sectional area as well as a very efficient means of water cooling, all solder joints being in direct contact with the cooling water.

Surrounding the crucible–radiator combination are two concentric tantalum heat shields. These shields are spot welded to stainless steel rings. The heat shield plus ring assembly fits snugly onto the back plate of the oven. The combination of rigid attachment and cooling by thermal conduction to the water cooled back plate greatly extends the

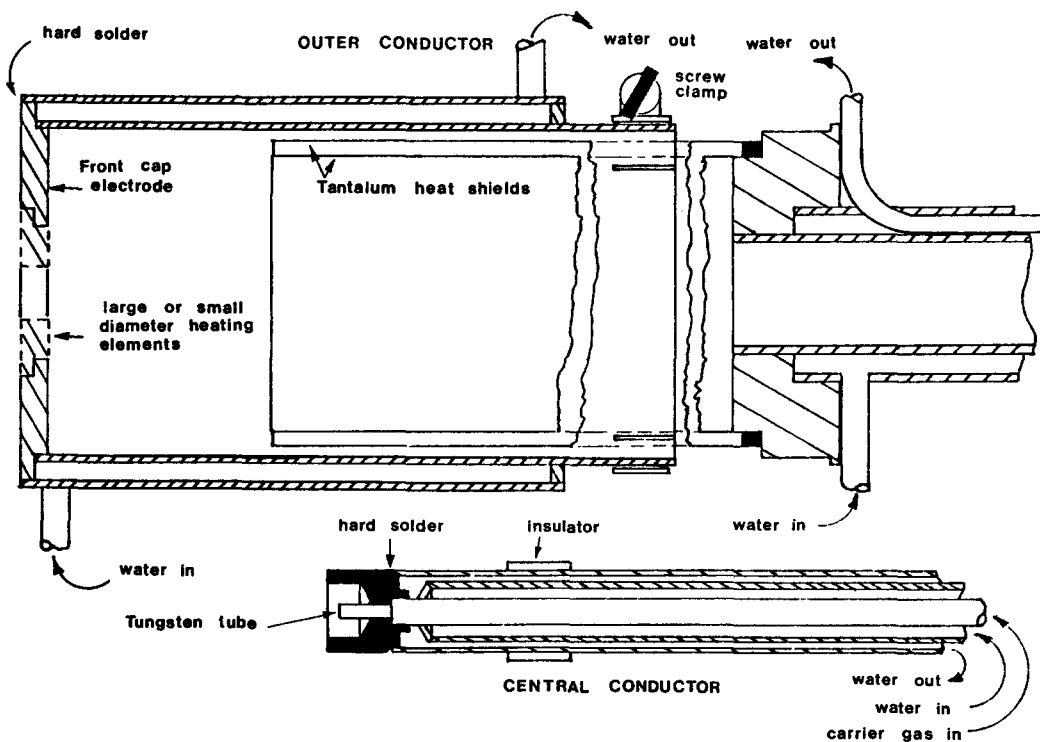


FIG. 6. Copper oven, full scale section along center line.

working life of the tantalum heat shields. Heat shields will often fail in oven designs which do not supply adequate support or heat removal, tantalum, among several high temperature metals, becoming very brittle, distorting, and/or cracking on cooling. The average heat shield life in this oven corresponds to 50 experiments of 2–3 h duration at 2100–2800 K. The entire assembly described above was housed in a double walled, water cooled copper jacket.

Oven designs are routinely plagued by heating element failure when support electrodes move relative to each other, and, in addition, thermal expansion can also produce sufficient force to induce cracking of the element. In the present design, the electrodes cannot move relative to each other once the oven is assembled. However, the central electrode can be slid backward or forward during the loading to accommodate different sizes of heating element. The heating element is held in place by a slight friction fit between the electrodes and the element (interference fit ≈ 0.0005 in.). No clamps are used to hold the heated crucible and radiation elements in place. A friction fit is adequate to hold the heating element in position and is superior to clamping for electrical contact. The friction fit also minimizes the effects of expansion and contraction produced by change in oven temperature.

Crucible and radiator designs: Temperature measurement

Figure 8 depicts several crucible and radiator designs used in the present experiments. Graphite is the major structural material used to make these components because of its acceptable resistivity and its ability to withstand high temperatures. However, if not properly chosen this material can be relatively porous to the diffusion of molten metal vapors and carrier gases through crucible walls (see also Fig. 7) making it difficult to maintain pressure behind the nozzle. Therefore, only high density graphite is used and, in certain cases, tungsten and tantalum inserts [Fig. 8(c)] are employed to aid in maintenance of backing pressures.

The radiator–crucible designs can be grouped into two limiting categories. Those constructions which employ a separate radiator and crucible (see Fig. 7) maintain radiative heat as the primary source of sample heating. In other configurations the crucible alone is the entire heating element. The oven jacket described in Figs. 6 and 7 is quite versatile, easily altered to meet the needs of an experiment, and operative in either the crucible only or crucible plus radiator mode. A typical thin-walled solid radiator is depicted in Fig. 7 whereas Fig. 8(f) corresponds to an alternate radiator design which proves most useful for maintaining the highest temperatures. It consists of a 1.23 in. o.d. graphite tube of 0.08 in. wall thickness; slots are cut into the radiator to provide a tenuous path for the conduction of electricity. High temperature testing of this slotted radiator showed that it could sustain temperatures well in excess of 2900 K with no damage to the oven. Several modifications of the solid and slotted radiator designs have been used in the formation and characterization of copper trimer.

Temperature measurements have been made in the system using optical pyrometry or employing tungsten

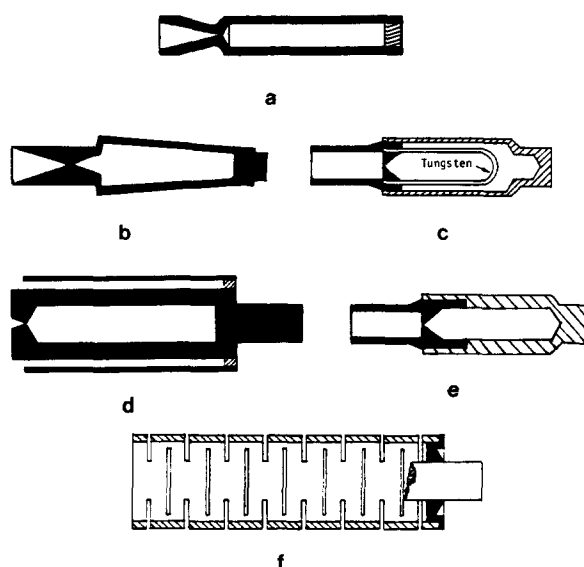


FIG. 8. Crucible and radiator designs for use with the copper oven system. (a) Crucible configuration used without radiator to obtain copper trimer hot band spectra in the region 16 500–17 800 cm^{-1} [Fig. 4(a)]. (b) Crucible configuration used without radiator to obtain copper trimer hot band spectra in the region 17 600–18 550 cm^{-1} [Fig. 4(b)]. (c) Tight configuration carbon + tungsten insert radiator + crucible design used to obtain the copper trimer excitation spectrum depicted in Figs. 2(c)–3(a). (d) Modified solid radiator–inner small crucible design used to obtain the cool copper trimer excitation spectrum shown in Fig. 2(b). (e) Modified all carbon tight crucible–radiator design used to obtain the copper trimer excitation spectrum depicted in Fig. 3(b). (f) Slotted radiator design with attachment to back inner electrode (Figs. 6 and 7) indicated.

sheathed tungsten–rhenium thermocouples (Omega engineering) connected to the front of the sample crucible as shown in Fig. 9. Temperatures up to 2800 K were measured using either technique.

Note: The oven system has been operated at temperatures approaching 3300 K with subsequent ablation of some carbon from the radiator and/or crucible materials. While initial measurements of temperature were made with the two techniques described, an alternate test of the slotted radiator

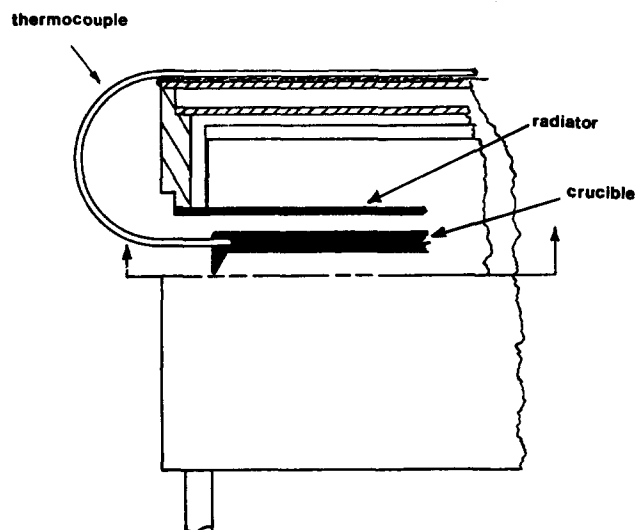


FIG. 9. Temperature measurement: Thermocouple insert in copper cluster oven.

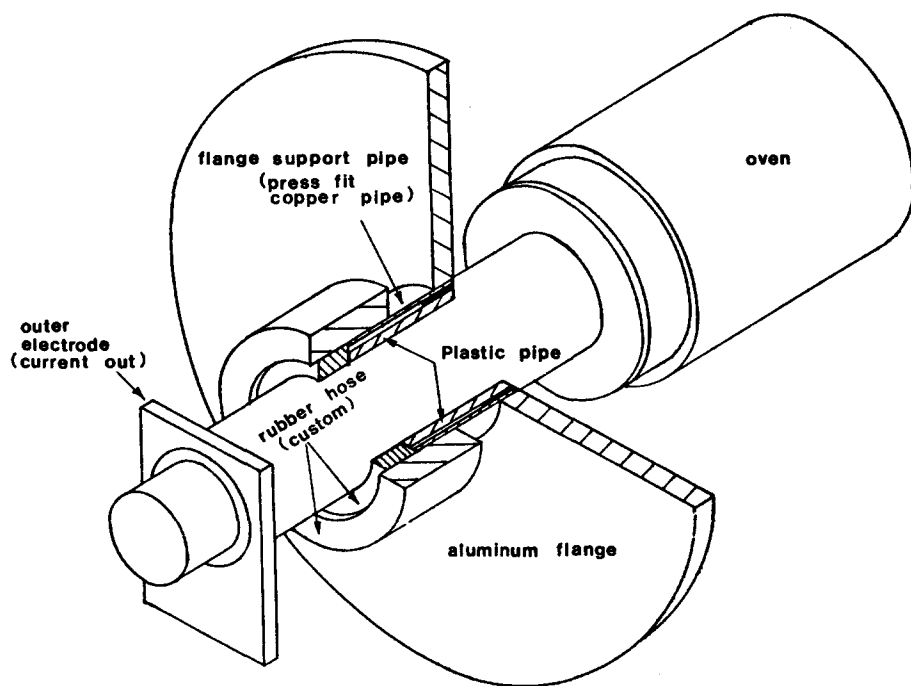


FIG. 10. Copper oven flange mount.

design involved the use of a crucible with several sample compartments containing different metals to be used as indicators of the temperature. The multisample crucible contained tungsten (mp 3550 K), tantalum (mp 3270 K), boron (mp 2300 K), and zirconium (mp 2125 K). Lower melting metals could be seen vaporizing rapidly from the oven as the temperature increased. After a period (~ 10 min) of full power operation, the oven was allowed to cool and then dismantled for inspection. Only the tungsten and tantalum compartments retained any sample. The tungsten sample (0.005 in. diam wire) remained solid but was very brittle after the heating and cooling. The tantalum sample (0.030 in. diam wire) had melted forming a pool at the bottom of the sample compartment.

Nozzle preparation

Nozzle orifices, typically 0.008 in. or less, were prepared using either commercial drill bits or specially prepared tungsten wires. The tungsten wire drills proved especially useful for drilling holes beyond the reach of the commercial drill bits. The tungsten wires (0.005 in. diam) were first prepared by cutting one end at a 45° angle. The cut end of the wire (~ 0.01 in.) was then crushed to form a symmetric shovel shaped tip. We have found that tungsten wires prepared in this fashion can easily drill holes in graphite 0.007 in. in diameter at a reach of 1.5 in.

Oven mounting

The oven was mounted to an aluminum flange (Fig. 10) in a manner which allowed back and forth movement without breaking the system vacuum. The "angle of attack" of the oven could also be changed by as much as 7° in two dimensions while operating. The freedom of motion provided by the flange mount shown in Fig. 10 thus allowed ready fine adjustments to the oven's position.

Pressure sealing and electrical insulation were combined in the flange mount and oven employing a series of custom designed rubber gaskets. These gaskets were constructed from rubber hose, cooled to LN_2 temperature, spun on a lathe, and ground into shape with a high speed grinder. The main electrical insulation and support between the oven and mounting flange is a plastic pipe sliding over the oven shaft and into a copper flange support pipe. Rubber hose (Fig. 10) acts as the connection between the oven shafts, flange pipe, and customized rubber gaskets. The copper support pipe is pressed into the 1/2 in. thick aluminum mounting flange (0.004 in. interference fit) and sealed with Silastic RTV silicone rubber.

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- ¹⁸Barring extremely unusual selection rules, the hot band rotational temperature must be considerably lower than the effective vibrational temperature in Figs. 4(a) and 4(b) in order that we clearly observe fluorescence features depicted in these figures. However, the question of increased resolution due to a rotational cooling cannot account for the very different excitation groupings observed in these figures.
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- ²⁹Here, we simply note that the effective potential changes greatly, for those vibronic modes associated with the coupling of bending and asymmetric stretch modes, at very low energy if the pseudorotation barrier is low. On the other hand, a 350 cm^{-1} symmetric stretch frequency for the ground state of copper trimer is substantial but not so large as to suggest that the regions probed in this study (max level populated $\sim v'' = 6$) will involve serious deviations from a weakly anharmonic potential. The excitation inherent in the hot band spectra in Fig. 4(b) ($\sim 2000\text{ cm}^{-1}$) is substantially lower than the predicted bond energy of copper trimer ($\sim 16\,000\text{ cm}^{-1}$ —see Ref. 1).