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Luminescence of mass-selected CuAg in argon matrices

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Abstract

We report on an observation of the luminescence spectrum of mass-selected CuAg in an argon matrix. Although no Raman spectrum is obtained, an emission progression up to $v'' = 5$ is observed, corresponding to the $A0^+-X^1\Sigma^+$ transition observed in the gas phase. The origin of the transition is determined to be $20\,262(10)\text{ cm}^{-1}$. We obtain a value of $\omega_e'' = 223.8(4.9)\text{ cm}^{-1}$, which is consistent with the gas-phase observations.

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1. Introduction

In this Letter, we examine the spectroscopy of the heteronuclear dimer molecule copper–silver. Much of our previous work concentrated on homonuclear clusters [1]. The heteronuclear molecule CuAg is one of the simplest transition metal dimers, since it is formed from atoms with filled d subshells. Several spectroscopic experiments on gas phase CuAg [2,3] have been carried out. Bishea et al. [2] used resonant two-photon ionization spectra to analyze jet-cooled diatomic CuAg and obtained $\Delta G''_{1/2} = 229.17\text{ cm}^{-1}$. This was based on observation of only one hot band in the ground state, although transitions to numerous excited states were both vibrationally and rotationally resolved. They assigned the ground state to $X^1\Sigma^+$,

corresponding to a molecular configuration of $3d_{\text{Cu}}^{10}4d_{\text{Ag}}^{10}\sigma^2$, with an observed bond length of $r_e'' = 2.3735\text{ Å}$. From the emission spectrum of CuAg in the visible region, Joshi and Majumdar [3] found a ground-state vibrational frequency of $\omega_e = 231.8\text{ cm}^{-1}$ and $\omega_e x_e = 0.80\text{ cm}^{-1}$.

In this Letter, we report on an observation of the luminescence spectrum of mass-selected CuAg in an argon matrix. Although no Raman spectrum is obtained, a fluorescence progression up to $v'' = 5$ is observed, corresponding to the $A0^+-X^1\Sigma^+$ transition observed in the gas phase. We obtain a value of $\omega_e = 223.8(4.9)\text{ cm}^{-1}$, which is consistent with the gas-phase observations.

2. Experiment

The absorption and resonance Raman spectrum of mass-selected CuAg clusters were acquired using the CCNY metal cluster deposition source.

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The design of this apparatus has been discussed in detail in other publications [4,5] but will be described briefly here. An argon ion beam of 10 mA (at 25 keV) sputters a water-cooled CuAg target (Goodfellow, 72:28% in molar ratio Ag:Cu. The melting point is of the sample 779 °C).

In the beam, the metal target was maintained at about 300 V. A series of einzel lenses collects the sputtered metal cluster ions from the metal sputtering region, and a Wien filter mass selects the focussed cluster ions. Any neutral atoms or clusters produced during the sputtering process that pass through the mass selector are removed by a 10° bend in the path following the Wien filter. A second set of einzel lenses focuses the mass-selected cations into the deposition region, which are then codeposited with argon gas and electrons, for neutralization, onto a CaF₂ substrate. A cryostat cools the substrate to ~16 K. To prevent degradation upon impact with the CaF₂ substrate, focussed ions are slowed to ~10 eV to ensure a soft landing on the substrate. The metal cluster/Ar matrix had a growth rate of ~6 μ/h. The argon:cluster ratio was ~10⁴:1. Several deposits were carried out, during which the current for a particular mass-to-charge (M/C in amu/electron charge) ratio was optimized. For M/C = 170 the optimized current was 35 nA for CuAg⁺. Since the resolving power of our Wien filter is relatively low (around 6–7) in order to attain high throughput, we cannot adequately separate the homonuclear dimers Cu₂ (130 amu) and Ag₂ (215 amu) from the mixed dimer. However, the spectra of the former are well known, and in any case, the spectra of both Cu₂ and Ag₂ are relatively weak, so that we have had no trouble obtaining unambiguous emission spectra desired. We may then use the luminescence excitation profile obtained to confirm at least partially, the assignment of the absorption spectrum.

Optical emission spectroscopy was carried out in situ on the matrix sample. An absorption spectrum, in the form of a 'scattering depletion spectrum' (SDS) was also obtained. The 'SDS' absorption is a ratio between scattered light from the edge and center, where most of the sample is deposited, to that of the CaF₂ substrate. The scattered light is collected at a 90° angle from the incident radiant.

The visible lines of a Spectra Physics 2045 argon ion laser were used to observe emission features of the mass-selected species. The laser power incident on the sample was typically about 50 mW. Plasma lines from the laser were removed by predispersing the laser beam with a diffraction grating. The 327 cm⁻¹ line of the CaF₂ substrate was used to calibrate all spectral shifts. The detection system consists of a Spex 1877E 0.6m Triplemate Spectrometer coupled with a liquid nitrogen cooled CCD system (Spectrum One and CCD30). The computer software DM3000R was utilized to acquire, interpret and display spectral information from the CCD.

3. Results and discussion

The SDS (absorption) spectrum of CuAg is shown in Fig. 1. Since there is no spectroscopic evidence to support the existence of much copper dimer or silver dimer from the Raman spectrum, we conclude that the SDS spectra of the CuAg deposit represents contributions from the CuAg dimer, and to a lesser extent atomic copper and silver produced by fragmentation of dimers on deposition. The weak absorption lines between 300 and 330 nm are mainly due to the contribution of

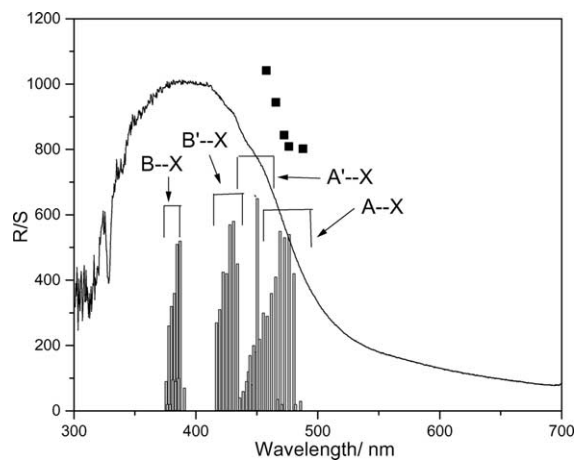


Fig. 1. Scattering depletion spectrum (SDS) of CuAg. Also shown is the gas-phase data from Bishea et al. [2]. Insert curve (■) is the luminescence excitation profile for the 19813 cm⁻¹ emission line.

Cu and/or silver atoms [6,7], and we infer that the fragmentation of CuAg is about 25%. The extent of fragmentation on deposition may be estimated by comparing the intensities of atomic excitation features in a dimer deposition with those obtained from depositions of the atom under similar conditions. Fig. 1 also shows, for comparison, a bar graph illustrating the results of Bishea et al. [2] in the gas phase. We can see that despite the considerably lower resolution afforded in this experiment, there is general agreement between the results of both experiments. The dotted curve in Fig. 1 shows the luminescence excitation profile of the line at 19813 cm⁻¹, and this further confirms our assignment of the band to CuAg.

No Raman signal was observed because a much stronger luminescence is obtained when exciting with an argon ion laser. Fig. 2 shows the laser excited fluorescence spectra of CuAg excited at 457.9 nm. A vibrational progression with spacing approximately 224 cm⁻¹ can clearly be discerned. The average emission frequencies are listed in Table 1. The data represents averaged emission frequencies from four different excitation wavelengths (457.9, 465.8, 472.8, and 476.5 nm). These frequencies were obtained by using a least-squares fitting routine, with a set of four or five Gaussian functions, and the uncertainties listed represent the full-width of the function used in the optimized fit.

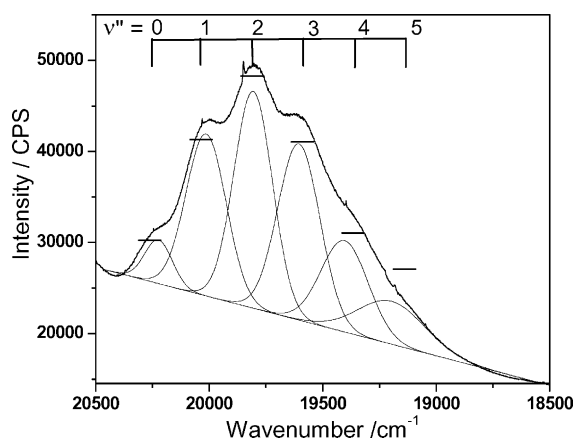


Fig. 2. Laser excited fluorescence spectra of CuAg in an argon matrix excited with the 457.9 nm argon ion laser line. The horizontal lines represent the calculated Franck-Condon factors.

Table 1
Observed emission frequencies of CuAg

Assignment ($v'-v''$)	Frequency (cm ⁻¹)	$\Delta G(v'' + 1/2)$
0-0	20 262 (220)	226
0-1	20 036 (250)	223
0-2	19 813 (270)	223
0-3	19 590 (270)	223
0-4	19 367 (250)	227
0-5	19 140 (300)	

The Franck-Condon envelope of intensity of the progression indicates that there is a considerable change in internuclear distance between the two electronic states involved in the transition. The location of the transition, and the approximate vibrational spacing indicates that it most likely corresponds to the $A0^+-X^1\Sigma^+$ transition observed in the gas phase by Bishea et al. [2]. They found a spectroscopic origin at 20 807 cm⁻¹ for this transition, and were able to observe only the first hot band from the ground state, with $\Delta G''_{1/2} = 229.17(28)$ cm⁻¹. From a rotational analysis they found that the equilibrium internuclear distances in the two states were $r'_e = 2.522(2)$ Å and $r''_e = 2.3732(8)$ Å, respectively. Utilizing this information, and assuming that matrix effects are small, we may assign the observed emission spectrum. The most intense band in our spectrum (at 19 813 cm⁻¹) is expected to be that vibration for which the ground state potential curve lies directly below the potential minimum of the excited state. Initially, we take the harmonic oscillator approximation, and solve the equation $(v + 1/2)\hbar\omega_e = 1/2k_e(r'_e - r''_e)^2$ for the unknown v . Taking $\hbar\omega_e'' = 229$ cm⁻¹ and $k_e = 1.24$ mdyn/Å we obtain $v'' = 2.5$. Using a more sophisticated method, assuming a Morse potential function: $V(r - r''_e) = D_e(1 - e^{-\beta(r - r''_e)})^2$ for which $\beta = 1.2177 \times 10^7 \omega_e \sqrt{\mu/D_e}$, we obtain graphically $v'' = 2.0$, and we assign this to the most intense peak observed. The resulting assignments are shown in Fig. 2, and listed in the table. The origin of the transition is determined to be 20 262 (10) cm⁻¹, in reasonable agreement with that of Bishea et al. [2]. Note also that our observed value of the spectral origin is shifted about 545 cm⁻¹ to the red of the gas phase values. Since there are so few examples of

transition metal diatomic emission spectra, it is difficult to know if this is typical. However, for Pt_2 we obtained a blue shift [8] of 503 cm^{-1} .

This assignment enables us to fit the observed values of $\Delta G(v'' + 1/2)$ by standard techniques to obtain $\omega_e = 223.8(4.9)\text{ cm}^{-1}$. These were obtained by averaging over the spectra obtained at four different wavelengths, and the deviation reported here is in that average. (We have excluded the $v'' = 5$ line from this fit, since it is so poorly determined, and only observed clearly in one spectrum.) This value can be seen to be in excellent agreement with that observed in the gas phase, and this may be taken as further confirmation of our assignment. From the observed value of the vibrational frequency we may determine the force constant to be 1.18 mdyn/\AA . This is also in good agreement with previous determinations. The observed force constant of the mixed dimer CuAg ($k_e = 1.18\text{ mdyn/\AA}$ in Ar matrix, 1.24 mdyn/\AA in gas phase) is found to lie between those of the component homonuclear dimers Cu_2 ; $k_e = 1.33\text{ mdyn/\AA}$ and Ag_2 ; $k_e = 1.18\text{ mdyn/\AA}$.

We can obtain further confirmation of our assignment by obtaining a Franck–Condon analysis of the observed spectra. We utilize an excited state potential function with terms up to fourth power in the internuclear distance, and include the values of ω_e and $\omega_e x_e$ for the excited state obtained from the gas phase results [2]. For the ground state we used a simple harmonic oscillator, since there is little evidence for anharmonicity. We took the value of Δr_e to be an adjustable parameter, and obtained an optimum fit to the intensity envelope

shown in Fig. 2 by the horizontal lines. The value of $\Delta r_e = 0.156\text{ \AA}$ is quite close to the gas phase value of 0.149 \AA obtained by Bishea et al. [2].

In summary, we have obtained an emission spectrum of mass-selected CuAg in argon matrices. A progression was observed up to $v'' = 5$, corresponding to the $\text{A}0^+ - \text{X}^1\Sigma^+$ transition observed in the gas phase. The origin of the transition is determined to be $20262(10)\text{ cm}^{-1}$. We obtain the value of $\omega_e = 223.8(4.9)\text{ cm}^{-1}$, which is consistent with the gas-phase observations.

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