Laser Photodissociation Spectroscopy of Mass-selected Metal Clusters

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Electronic spectra are reported for the metal cluster (Te$_2^+$) and metal cluster complex (Ag$^+$-benzene, Mg$^+$-CO$_2$) cations. These ions are generated by laser vaporization in a pulsed nozzle source, jet-cooled, mass-selected with a reflectron time-of-flight spectrometer, and dissociated on resonance with a tunable dye laser. Electronic excitation spectra are recorded by monitoring the appearance of the fragment-ion channel(s) as the dissociation laser is tuned through electronic and/or vibronic resonances. Analysis of these new spectra yields vibrational constants, binding energetics and evidence for new photochemistry in these novel ion systems.

The electronic structure and chemical bonding in gas-phase metal clusters continue to be poorly understood, primarily because of insufficient spectroscopic data. There is simply no spectroscopic method presently available with the sensitivity and selectivity required to study species produced in low density molecular beams in a distribution of sizes. Highly sensitive spectroscopic methods, such as laser-induced fluorescence (LIF) and resonant two-photon ionization (R2PI), have been applied in previous cluster studies.$^{1}$ However, these techniques are often undermined by the complex photophysics occurring in excited cluster electronic states (curve crossings, predissociation etc.). Most clusters do not fluoresce with appreciable quantum yields and they are difficult to ionize efficiently without fragmentation. Consequently, there are few spectroscopic measurements for aggregates larger than two or three atoms. This limited data makes it difficult to interpret other fascinating cluster phenomena, such as size-specific reactivity, which are expected to be strongly influenced by structure. It is increasingly clear that new spectroscopic tools are needed in cluster research.

In the present report, we describe the application of resonance enhanced photodissociation (REPD) to the spectroscopy of mass-selected cluster cations and novel ion-molecule cluster complexes. REPD spectroscopy has been described previously for organic molecular cations by several research groups,$^{2-6}$ including Maier and co-workers$^{2-3}$ and Schlag and co-workers.$^{4-5}$ This research indicates that REPD can provide vibrationally and rotationally resolved electronic spectra for ions which cannot be studied by other techniques. The method is particularly attractive for cluster ions, which can be mass-selected from the distribution of sizes produced by typical cluster sources. Structured dissociation spectra have in fact already been observed for transition metal dimer cations (Fe$_2^+$ and Nb$_2^+$) by Smalley et al.$^7$ but these spectra could not be assigned. Jarrold has recently described structureless dissociation spectra for aluminium clusters$^8$ and a spectrum for the copper tetramer cation with partial vibrational resolution.$^9$ Brucat has reported the vibrationally resolved dissociation spectrum for Ni$_2^+$. Together with these other recent results, the data presented here provide some of the first applications of the REPD method to metal cluster spectroscopy.

This paper describes three examples of ion spectroscopy systems studied with the REPD method, Te$_2^+$, Mg$^+$-CO$_2$ and Ag$^+$-benzene. In the case of Te$_2^+$, a vibrationally resolved spectrum allows determination of spectroscopic constants in the ground and
excited state. The Mg\(^+\)-CO\(_2\) complex exhibits partially resolved structure in two different product channels, demonstrating the occurrence of an unusual photo-induced reaction within the ion-molecule complex. The Ag\(^-\)-benzene complex likewise exhibits unusual photochemistry, but in the form of intra-cluster charge transfer during dissociation. These new systems illustrate the variety of cluster spectroscopy and photochemistry experiments which can be investigated by this photodissociation method.

**Experimental**

Clusters and cluster complexes for these experiments are produced by laser vaporization. The pulsed-nozzle cluster source and molecular beam apparatus used are described in detail in previous reports from our research group.\(^{11}\) Vaporization is accomplished with an excimer laser (Lumonics) at 308 nm or a Nd:YAG laser (Spectra Physics) at 532 nm. Ionized clusters condense directly from the laser plasma and are jet-cooled in expansions of helium, argon or helium-argon mixtures as they exit the cluster source. Cluster complexes with stable molecules are formed in expansions of rare gas seeded with the molecule of interest. The supersonic expansion produced is believed to constitute a neutral plasma with a net balance of positive and negative charges. This expansion can therefore traverse the molecular beam apparatus, including a 5 mm skimmer, without serious density losses from coulomb repulsion.

At a point 40 cm downstream, the skimmed molecular beam enters the source region of a home-made reflectron time-of-flight mass spectrometer. The design of this instrument, and its application for mass-selected cluster photodissociation experiments, has been described previously by our group.\(^{12}\) The schematic diagram of this spectrometer for ion spectroscopy experiments is shown in Fig. 1. Cold clusters are extracted from the molecular beam with pulsed acceleration voltages. The desired cluster is then mass-selected by its time-of-flight through an initial drift tube section. Undesired clusters are rejected, and the selected size transmitted, with pulsed deflection plates located just before the reflectron assembly. Pulsed excitation with a tunable Nd:YAG pumped dye laser (Spectra Physics PDL-2) occurs as the selected ion packet reaches its turning point in the reflectron field. Parent ions and their photoproducts are mass analysed by their flight time through the second drift tube section. Resonance-enhanced dissociation spectra are recorded by monitoring the fragment-ion intensity as the dissociation laser is scanned.

**Results and Discussions**

**Diatomic Tellurium Cation**

Small Te molecules have been studied previously in the equilibrium vapours sampled from high-temperature ovens.\(^{13}\) Initial MS measurements gave the dissociation energy for Te\(_2\) (2.677 eV) and the appearance potential for Te\(_{1}\) (8.3 eV). When these numbers are combined with the atomic ionization potential, a dissociation energy of 3.40 eV is obtained for Te\(_{1}\). This system follows the same trend observed for the other Group 16 diatomic molecules in that the ion is more strongly bound than the corresponding neutral. Recent cluster ion MS experiments and mass-selected photodissociation experiments in our group find that Te\(_{2}\)\(^+\) is produced preferentially in both the condensation and dissociation of Te molecules, also consistent with its relative stability.\(^{14}\) These experiments find that Te\(_{2}\)\(^+\) dissociates at the ultraviolet laser wavelengths of 355 and 308 nm. Photoelectron spectroscopy of high-temperature vapours has determined the Te\(_2\) excited electronic molecular orbital energies.\(^{15-17}\) By analogy to the other Group 16 diatomics, the ground state has been assigned as \( ^{2} \Pi \) with a spin–orbit splitting of 0.47 eV. New photoelectron experiments employing supersonic cooling have obtained vibrationally resolved spectra, revealing the ground-state vibrational frequency
Fig. 1 The reflection time-of-flight mass spectrometer configuration used for ion dissociation spectroscopy. Cluster ions formed by laser vaporization are accelerated into the reflectron, size-selected at the pulsed mass gate, and irradiated at the turning point in the reflectron. Fragment ions are detected as a function of wavelength to record a spectrum.

The excited electronic energy levels measured for Te$_2^+$ in photoelectron experiments suggest that there should be an optically allowed $A^2\Pi_u \leftarrow X^2\Pi_g$ transition at visible wavelengths in the 670–680 nm region. Single-photon excitation in this wavelength region is not energetic enough to cause dissociation in Te$_2^+$ on the ground-state potential-energy surface, but absorption of two or more photons may cause dissociation on a suitable excited-state potential surface.

As shown in Fig. 2, laser excitation of mass-selected Te$_2^+$ in this wavelength region does result in photodissociation. The wavelength dependence of the Te$^+$ fragment ion produces a structured spectrum, with spacings characteristic of a vibrational progression. As described above, this dissociation spectrum must be the result of absorption of at least two photons. However, the efficiency of this absorption process indicates that it results from a single-photon resonance. Using the measured laser intensity and parent ion beam depletion, we estimate that the peak cross-section for photodissociation is ca. $10^{-18}$ cm$^2$. Therefore, we conclude that the observed spectrum is the result of resonance-enhanced multiphoton absorption, with the resonance occurring at the one-photon level. We assign the structured features to the vibrationally resolved $A^2\Pi_u \leftarrow X^2\Pi_g$ transition expected in this wavelength region. Except for the excited $^2\Sigma_g^-$ state observed in
the photoelectron spectrum, there is no information available for higher excited electronic states. However, the $^2\Sigma^-$ state is at the approximate energy to be accessed resonantly at the two-photon level with the laser frequency used here. We must assume that the dissociation event occurs in either this state or a higher one, but the exact mechanism (predissociation or direct dissociation) is not known.

Wavelength scans over five overlapping dye and dye mixture tuning regions are summed and connected via computer to produce the composite photodissociation spectrum shown. Band intensities are not corrected for the laser power variation within or between dye curves. As shown, the widths of vibrational bands (15-20 cm$^{-1}$) are significantly broader than that of the laser (0.5 cm$^{-1}$). However, Te has seven naturally occurring isotopes with significant abundance, and the distribution of isotopes in the dimer mass channel is not resolved by our mass selection. Therefore the vibrational bands are broadened by the isotope shifts, as well as rotational band profiles.

The vibrational-line positions obtained are shown in Table 1, with frequencies quoted relative to the origin band at 14 755 ± 10 cm$^{-1}$. As indicated, we assign the observed bands to a main excited state progression originating in $v'' = 0$, and a weaker progression originating in $v'' = 1$. A least-squares fit of these band positions yields an excited state vibrational frequency of $\omega_e' = 199.4 ± 2.0$ cm$^{-1}$ and an anharmonicity of $0.46 ± 0.13$ cm$^{-1}$. Bands are observed in these progressions up to 2690 cm$^{-1}$, placing a lower limit on the excited-state binding energy. However, the long regular progression and low anharmonicity suggest that the actual dissociation energy is significantly greater than this value. A simple fit of the progression to a Morse potential produces a dissociation energy ($D_e$) in the excited state of 2.27 eV, but because this fit uses only low vibrational bands it is not expected to be highly accurate. From the 'hot' vibrational bands observed, we obtain a ground-state vibrational frequency of $\omega_e'' = 279 ± 17$ cm$^{-1}$. This value is in excellent agreement with that obtained by Shirley et al. (282 cm$^{-1}$) in photoelectron experiments. The anharmonicity in the ground state cannot be calculated with any confidence, since there is only one vibrational band with $v'' > 1$. All errors in calculated band positions using these constants are smaller than the corresponding spectral linewidths.

The data presented here are consistent with a simple bonding picture for Te$_2^+$. The $^2\Pi_{g,1/2}$ ground state assigned from the photoelectron data has the configuration...
Table 1 Observed and calculated vibrational band positions for the Te₂⁺ A²Π_u ← X²Π_k,½ system detected by resonance-enhanced dissociation spectroscopy

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\(^a\) Relative to the 0–0 band at 14 755 ± 10 cm\(^{-1}\). \(^b\) Calculated using the parameters: \(\omega_0 = 199.4\), \(\omega_e x'_e = 0.46\), \(\omega_e^\prime = 279.0\), and \(\omega_e x'_e^\prime = 5.2\) cm\(^{-1}\).

\((5s\sigma_u)^2(5s\pi_u)^2(5p\pi_u)^4(5p\pi_g)^1\) with a bond order of 2.5. The ion excited state arises from excitation of a bonding 5p\(\pi_u\) electron to the antibonding 5p\(\pi_g\) orbital, reducing the bond order to 1.5. A reduced vibrational frequency (199 cf. 279 cm\(^{-1}\)) and dissociation energy in the excited state are therefore not surprising for this system.

**Magnesium–CO₂ complex**

Complexes of metal ions with rare-gas atoms or small molecules have recently been produced in laser vaporization sources. We produce complexes of the form Mg⁺–(CO₂)\(_x\) by expansion of a mixture of CO₂ in helium through the usual cluster source. Studies on complexes such as these make it possible to investigate the role of 'solvation' on cluster spectroscopy and photochemistry. In these complexes the charge is expected to be localized on the metal atom because it has a significantly lower ionization potential than the molecular species present. The magnesium ion is particularly interesting as the metal seed in these systems because it has an ultraviolet atomic resonance (²S-²P₀ at 279.7 nm) which can be used as a chromophore for efficient complex excitation. We expect to see absorption near this resonance for magnesium ion complexes, with spectral shifts depending on the relative strength of interactions in the ground and excited states. Vibrational-band structure may also be found under favourable circumstances.

The photofragment excitation observed for the complex Mg⁺–CO₂ is shown in the two spectra in Fig. 3. The complex exhibits both the characteristics of spectral shifting because of complexation and partially resolved vibrational-band structure. Additionally, the complex dissociates via an interesting photochemical pathway. Cleavage of the electrostatic bond is the expected dissociation path for an ion–molecule complex such
Fig. 3 The photodissociation spectra obtained for the Mg$^+$-CO$_2$ complex near 280 nm in the Mg$^+$ and MgO$^+$ fragment channels. The zero point on the frequency axis is at 278.25 nm.

as this, and this channel accounts for \textit{ca.} 50\% of the fragmentation in Mg$^+$-CO$_2$. The unexpected fragment channel, also occurring with \textit{ca.} 50\% yield, is formation of MgO$^+$. As shown in Fig. 3, the wavelength dependence of these fragmentation channels exhibits some structure resembling vibrational bands. While the apparent peaks are broad and ill-defined it is clear that both fragment channels have the same wavelength dependence. This establishes that both fragment channels are derived from the same parent complex. Since absorption occurs at the magnesium ion resonance, the common parent complex must be excited Mg$^+$-CO$_2$. The mechanism for this photochemistry is therefore absorption by the ion-molecule complex followed by an intra-complex reaction to form the metal oxide ion. This reaction is endothermic in the ground state, but is made possible by the 4.4 eV electronic excitation. While there are other examples of rearrangement reactions within ion-molecule complexes,\textsuperscript{18} photochemistry in metal ion complexes such as this is virtually unstudied. However, Brucat and co-workers have recently observed a similar excited state reaction in V$^+$-CO$_2$.\textsuperscript{19}

The lowest energy band apparent in these excitation spectra appears \textit{ca.} 200 cm$^{-1}$ to the blue of the atomic transition. If this band is the origin of the complex electronic
transition, the complex must bound more strongly in its ground state than it is in the excited state. Metal-CO$_2$ vibrational stretching and bending modes could in principle be observed in the spectrum at low energy, while CO$_2$ modes would be at intermediate (bend) and much higher (stretch) frequencies. Assuming that the first apparent band is indeed the origin, a low-frequency spacing to the first weak feature would be ca. 100 cm$^{-1}$ and a higher frequency spacing to the first stronger feature would be ca. 300 cm$^{-1}$. Bauschlicher have recently calculated the structure of this complex to be linear, with bending and stretching frequencies of 77 and 250 cm$^{-1}$. While the similarity of these frequencies to those observed is close, this should not be considered significant until better quality spectra can be obtained.

It is unclear as yet why the spectra have such broad bands, and why the signal levels on resonance are so small. If the precursor ions are internally hot, rotational structure could broaden the bands. If dissociation is fast, the bands might be lifetime broadened. If there is a significant geometry change between the ground and excited state, a Franck-Condon effect may cause the first observable bands to occur well above the electronic origin in a region of overlapping vibrational bands. Unfortunately, it is impossible at present to determine the source of the spectral complexity. Nevertheless, even the partially resolved structure is enough to give us some insight into the photochemical dynamics in these ion-molecule complexes.

**Silver–Benzene Complex**

Silver–benzene complexes of the form (Ag$_x$-benzene$_y$)$^+$ are produce in our pulsed nozzle source by vaporization of silver in an expansion gas of helium seeded with room temperature benzene vapour. As described above, the charge in these systems is localized on the metal because of its lower ionization potential. When complexes are formed with silver atomic ions, the expected electronic structure of the complex is particularly simple. Unlike the magnesium ion, Ag$^+$ has no atomic resonances at low energy because of its closed-shell d$^{10}$ electronic configuration. The isolated benzene molecule absorbs in its $\pi-\pi^*$ electronic transition, but only above 260 nm. At first glance, it would seem that the Ag$^+$-benzene complex would not absorb light at low energy. However, as shown in Fig. 4, this complex does absorb and dissociate at low energy. The surprise
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is that the fragment of Ag\(^{+}\)-benzene dissociation is not Ag\(^{+}\); it is the benzene cation, C\(_6\)H\(_6\)^{+}. This is the only fragment channel observed over the wavelength region between 700 and 266 nm.

Production of the benzene cation is not the lowest-energy dissociation process, because the charge is not on the species (Ag) with the lowest ionization potential. This process can occur, however, in an excited electronic state correlating to Ag\(^{2}\)S) and ground-state C\(_6\)H\(_6\)^{+}. This excited electronic state is a 'charge-transfer' state, whose energy at the asymptote above ground-state silver ions (\(^{1}\)S) and neutral benzene corresponds to the ionization potential difference (\(\Delta E_i\)) between the silver atom (\(E_i = 7.58\) eV) and the benzene molecule (\(E_i = 9.24\) eV). Dissociation in the excited state can occur for either a bound excited state prepared above its dissociation limit or for a repulsive upper state excited anywhere along its surface. In either case, the final state is a continuum and a structureless spectrum is expected. Fig. 4 illustrates that continuous absorption is in fact observed above a threshold wavelength of 418 nm. At energies below this threshold, absorption in the complex may occur, but it cannot be detected in our experiment because there is no dissociation.

This charge-transfer photodissociation threshold can be used to determine the ground-state dissociation energy of the metal–benzene complex. Absorption in this complex originates in the lower levels of the ground-state potential well. For excited-state dissociation to occur, the photon energy must exceed \(\Delta E_i\) between the metal atom and benzene and the ground-state complex well depth. Franck–Condon effects, which are impossible to predict in advance, may cause the observed vertical threshold to be greater than or equal to the actual adiabatic threshold. Therefore, using the known \(\Delta E_i\) and the measured threshold, it is possible to determine an upper limit on the ground-state complex binding energy, \(D_0^b\):

\[
D_0^b \leq h\nu_{ct} - \Delta E_i
\]

Using the threshold measured for Ag\(^{+}\)-benzene at 418 nm, we derive an upper limit on its binding energy of 1.30 eV, or 30.0 kcal mol\(^{-1}\). For comparison with this value, Armentrout and co-workers have measured the dissociation in the ground state directly by collision-induced dissociation (CID).\(^{21}\) This process produces Ag\(^{+}\) and neutral benzene. The threshold obtained by this method is 33.5 kcal mol\(^{-1}\). This slightly higher value is not unreasonable, because CID typically produces thresholds higher than the actual bond dissociation energy.\(^{\dagger}\) Therefore, the near agreement of our values suggests that this charge-transfer method may be a useful one for obtaining energetic data for metal–organic complexes. The vertical threshold measured in our experiment must be very close to the adiabatic threshold. We have also observed charge-transfer dissociation in numerous other complexes (silver-toluene, silver-acetone, copper-benzene, iron-benzene etc.), and are in the process of threshold determination in these other systems.\(^{22}\)

Conclusion

We have used a new time-of-flight mass spectrometer configuration to mass select metal cluster cations and metal-containing ion–molecule complexes and to study their absorption spectra and dissociation dynamics. The systems studied range from a simple metal dimer (Te\(^{+}\)), in which detailed vibrational constant information is obtained, to magnesium–CO\(_2\) and silver–benzene ion–molecule complexes which exhibit new photochemistry. As illustrated by these studies, cluster ion photodissociation is a sensitive spectroscopic method for these systems and makes it possible to probe excited-state decomposition dynamics and ground-state thermochemistry. We suspect that further

\(^{\dagger}\) At threshold, energy transfer in CID collisions is not as efficient as at higher energy, resulting in the observation of high dissociation threshold from this method.
new insights will be obtained as we continue to explore this exciting new area of metal cluster research.

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