deuteration sensitive vibrations in BChl would be helpful in assigning its vibrations to a first approximation.

The effect of deuteration on the RR spectrum of BChl may be seen by comparing the spectrum in Figure 7a (fully protonated) with that in Figure 7b (fully deuterated). Both spectra were obtained on dry films. As may be seen, large differences exist between the two spectra and it is difficult in some cases to correlate the bands. Caution must be exercised as discussed in the case of Cu porphin where deuteration was found to produce either a decrease in a particular vibrational frequency (due to the pure isotope effect) or an increase in its value (because of a change in composition or form of the normal mode). With this caveat in mind, bands most sensitive to deuteration are tentatively identified as follows: 1609 (-12), 1589 (-51), 1286 (-26 or -47) (where the number given is the value (cm⁻¹) for the fully protonated form and the number in parentheses is the direction and magnitude of the shift on deuteration). A more detailed analysis of the effects of deuteration is underway.

Conclusions

The resonance Raman results presented here indicate that it is possible to distinguish certain types of BChl interactions through changes in its spectrum. In monomeric BChl systems, the most easily distinguished are coordination interactions. Two structure sensitive bands have been identified, band A (1609 cm⁻¹) and band B (1529 cm⁻¹). (A shoulder on band A near 1589 cm⁻¹ is also sensitive to coordination, but it is not well resolved.) The formation of six-coordinate BChl, through the interaction of two ligands at the central Mg atom, causes band A to shift 15 cm⁻¹ to lower frequencies for those modes which are most affected (Le., the methine vibrations which have expansion correlation which has been invoked to explain similar shifts in structure sensitive bands in a variety of porphyrins. In BChl the movement of its Mg atom into the plane of the macrocycle with an increase in coordination number should lead to an expansion of the porphyrin core. This expansion, in turn, results in an increase in bond length and a decrease in vibrational frequencies for those modes which are most affected (i.e., the methine C=C and pyrrole C=N stretching modes). In aggregated BChl systems, it has been observed that substantial differences are present in the RR spectra with respect to monomeric BChl, as well as between two of the three types of aggregates studied. In the pyrazine aggregate, formed through bifunctional coordination of pyrazine to Mg in BChl, both bands A and B indicate BChl is six-coordinate. Differences which are present between the RR spectrum of this aggregate and monomeric six-coordinate BChl include an enhancement of low-frequency modes between 600 and 700 cm⁻¹, which either are not observed or are extremely weak in monomeric BChl spectra, and an enhancement of the 1341-cm⁻¹ mode. The RR spectrum of a second type of aggregate, the BChl hydrate, is distinctive from both that of monomeric BChl and the pyrazine adduct. Both bands A and B are split, and band B is shifted to higher frequencies as compared to those of monomeric BChl. Shoulders on band A at 1637 and 1627 cm⁻¹ are characteristic of hydrogen-bonded C=O vibrations (the C-2 acetyl and C-9 keto). Hydrogen bonding of the C=O appears to enhance their RR scattering, perhaps through an increase in conjugation with the porphyrin π systems.

BChl interactions which produced much smaller changes in its RR spectrum include hydrogen bonding in monomeric solutions and self-aggregation. Hydrogen bonding in EtOH caused only a shift in the weak 1675-cm⁻¹ acetyl C=O band. Self-aggregation produced changes only in the relative intensities of the bands, especially that at 1609 cm⁻¹, resulting primarily from C=C stretching vibrations of the methines. It is possible, however, that greater effects in the RR spectrum of BChl as a result of hydrogen bonding or self-aggregation might be observed by using a different laser excitation wavelength. For example, excitation close in resonance with the Soret absorption bands produces stronger C=O scattering and would be more useful for studying hydrogen-bonding interactions.

In summary, the RR results discussed above are encouraging with respect to its potential application to the study of BChl interactions in vivo. Although reaction center and BChl protein complexes have already been examined by this technique, the effect of defined BChl interactions in vitro on its RR spectrum has not been examined in detail.

Acknowledgment. The authors wish to express their appreciation for financial support from NIH (Grant SR01 GM27498). T.M.C. acknowledges support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation. The deuterated BChl sample was provided by Dr. Marion Thurnauer.

Secondary Ion Mass Spectrometry of Small-Molecule Solids at Cryogenic Temperatures. 2.1 Rare Gas Solids

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Abstract: Secondary ion mass spectra of neat solid argon, krypton, and xenon were measured as a function of the nature and energy of the primary ions, He⁺-Xe⁺. With primary ions of large momentum, considerable quantities of large cluster ions of the matrix material are produced.

In secondary ion mass spectrometry (SIMS), the surface of a solid is bombarded by a beam of primary ions and the positive or negative secondary ions emitted from the solid are analyzed by a mass spectrometer. SIMS has been a very useful tool for examining surfaces as well as the bulk of metallic and ionic solids. More recently, its utility for molecular solids of low volatility has begun to be explored. Recently, it was also used to obtain the


(30) Lutz has investigated some of the effects of BChl interactions on its RR spectrum in ref 10b.
mass spectrum of a compound isolated in argon matrix.\textsuperscript{5,6} The wide-ranging potential of the method is becoming generally recognized and has been summarized recently.\textsuperscript{7}

In view of these developments, it is unfortunate that little is known with certainty about the fundamental processes involved in the formation of secondary ions and their subsequent emission. It appears to us that in addition to theoretical work,\textsuperscript{8} it would be helpful to obtain SIMS results on solids composed of very simple molecules with simple fragmentation patterns, and this represents the subject of the present series of investigations.

In the present paper, we report our observations on rare gas solids. They provide the simplest examples of "molecular solids", particularly well suited for theoretical investigations, and are of interest as commonly used matrix materials for stabilization of reactive intermediates. If matrix isolation SIMS is to become a viable technique, the behavior of pure matrix materials clearly needs to be understood.

Experimental Section

The secondary ionization mass spectrometer was constructed of 304 stainless steel and is bakeable up to 200 °C (a cross section of the instrument is shown in Fig. 1). The ion gun is a Riber model CI-50R which is designed to provide ion beam densities from \(10^{14}\) to \(10^{15}\) ions/cm\(^2\) in the ion energy range of 500 eV to 5 keV. The ion gun is provided with a 2 mm diameter aperture between the gun vessel and the sample chamber through which the ion beam travels. This allows for the use of an efficient differentially pumped system such that pressures in the sample chamber can be maintained in the \(10^{-9}\) torr region while the ion gun is in use. The ion gun vessel is pumped with 100 L/s Pfeiffer turbomolecular pump which results in a base pressure in the \(10^{-9}\) torr region. The sample chamber is pumped by a sorption pump \(5 \times 10^{-9}\) torr as read on the gas used. Under these conditions, few doubly charged ions are obtained with an extranuclear laboratories quadrupole mass spectrometer equipped with an electrostatic Bessel box which acts as an energy prefilter. This energy analyzer selects a range of energies of the emitted secondary ions before injecting them into the quadrupole mass filter. The energy the analyzer selects can be varied between 0 and \(50\) eV for both positive and negative ions and allows one to obtain secondary ion energy distributions. The observed secondary ion energies contain an unknown additive constant due to biasing by the electron floodgun filament. Changing the bias causes a 1-2 eV displacement of the observed intensity distribution curves but does not affect their shapes. The full width at half maximum for the selected energy can be varied between 0.7 and 0.4 eV.

The quadrupole mass filter with the extranuclear high Q head model 14 allows for a mass range of from 2 to 1000 amu. With other high Q heads the mass resolution can be improved but the mass range is decreased. The primary ion beam was varied between He\(^+\), Ne\(^+\), Ar\(^+\), Kr\(^+\), and Xe\(^+\). The beams were produced by filling the ion gun vessel with the appropriate research grade gas at a pressure of \(8 \times 10^{-9}\) torr as read from the ion gauge attached to the vessel. The ions were formed by 50 eV electrons, using emission currents between 1 and 20 mA depending on the gas used. Under these conditions, few doubly charged ions are formed (none with He and Ne). With the ion gun operating under these conditions, projectile ion densities striking the target sample were maintained within the range from \(1 \times 10^{14}\) to \(3 \times 10^{15}\) ions/cm\(^2\).

The solid samples were formed by depositing the appropriate gas through a leak valve onto a copper sample plate attached to the cold end of an Air Products cryostat and maintained at a temperature of approximately 18 K. The gas samples were research grade (Matheson) and were not purified further except by freeze and thaw cycles in the introduction chamber. During the desorption, the sample chamber was maintained at a pressure of \(10^{-8}\) to \(10^{-9}\) torr. The sample thickness on the gas used. Under these conditions, few doubly charged ions are obtained with an extranuclear laboratories quadrupole mass spectrometer equipped with an electrostatic Bessel box which acts as an energy prefilter. This energy analyzer selects a range of energies of the emitted secondary ions before injecting them into the quadrupole mass filter. The energy the analyzer selects can be varied between 0 and \(50\) eV for both positive and negative ions and allows one to obtain secondary ion energy distributions. The observed secondary ion energies contain an unknown additive constant due to biasing by the electron floodgun filament. Changing the bias causes a 1-2 eV displacement of the observed intensity distribution curves but does not affect their shapes. The full width at half maximum for the selected energy can be varied between 0.7 and 0.4 eV.

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The quadrupole is uneven as a function of mass. Also, it should be noted that our energy filter mounted in front of the quadrupole transmits only a relatively narrow 1-2 eV range of secondary ion energies. Since the secondary ion energy distribution curves have a different shape for the monoatomic ion and for the cluster ions, particularly with the lighter primary ions as described below, the measured ion abundance ratios are distorted relative to true ratios of total ion yields.

When He⁺, Ne⁺, or Ar⁺ is the primary ion, the kinetic energy distribution for the secondary ions shows a trend already familiar from previous work on water and alkali halides: the distribution of cluster ions peaks at lower energies than that of the parent ion. Figure 4 shows this trend for Ar⁺ as the primary ion and gives the kinetic energy distributions for the secondary ions Ar⁺, Ar₂⁺, and Ar₃⁺. The Ar⁺ distribution is broad and has a maximum at about 4 eV, whereas the Ar₂⁺ and Ar₃⁺ distributions are narrower and have maxima at lower energies, 2.5-3 eV. However, this trend does not continue as the primary ion increases in mass and momentum. As is seen in Figure 4, when Xe⁺ is used as the primary ion, the energy distribution of the secondary ions Ar₂⁺ and Ar₃⁺ is broader than that obtained with Ar⁺ as the primary ion, but the distribution of the secondary ion Ar⁺ is of comparable width in the two cases. With Xe⁺ as the primary ion, the maxima are not as clearly separated as was the case when Ar⁺ was the incoming projectile. The behavior of Kr⁺ as a primary ion is intermediate between Ar⁺ and Xe⁺. The kinetic energy distribution of doubly charged secondary ions is the same as that of the singly charged atomic ions.

The primary ions, He⁺ to Xe⁺, are not observed in the secondary ion spectra, at least not until after some hours of bombardment. This does not contradict our previous observation of ion scattering spectra of low-temperature matrices since the energy filter which has now been incorporated in our instrument will exclude all ions of high energy (over 20 eV), such as those scattered by the surface layer.

A series of SIMS measurements was performed on krypton isolated in a matrix of argon at ratios 1:10, 1:50, 1:100, 1:200, and 1:500. With 3 keV Ar⁺ as the primary ion, mixed cluster ions Ar⁺Kᵣᵣ⁺ were observed to the experimental limit (m/e 1000) in addition to the usual clusters Arₓ⁺ and Krₓ⁺. With increasing matrix isolation, the relative abundance of clusters containing more than one krypton atom (in both the mixed clusters and the cluster of Krₓ⁺) decreased rapidly (Figure 5). At a matrix ratio of 1:500,

![Figure 2](image-url) Positive SIMS of solid krypton (18 K) over mass range of 500, using Ar⁺ primary ions at kinetic energies of 1 keV and 4 keV.

![Figure 3](image-url) Positive SIMS (low resolution mass scan) of xenon (18 K) with Ar⁺ primary ions at 4.0 keV impacting energy.

The spectra contain the expected peaks of the singly charged and, with less intensity, doubly charged monoatomic rare gas ion. The relative abundance of the latter is a sensitive function of the nature of the primary ion but appears to be little affected by its impact energy within the range 0.5-4.0 keV (Figure 1). The solid Ar matrix yields Ar⁺⁺ with the He⁺ and, weakly, with Ne⁺ bombardment. Solid Kr and Xe matrices yield Kr⁺⁺ and Xe⁺⁺, respectively, with He⁺, Ne⁺, and Ar⁺ bombardment.

In addition to monoatomic ions, the mass spectra contain cluster ion peaks, whose relative intensity increases as the primary ion is changed in the series He⁺···Xe⁺ and as its impact energy is increased. The largest clusters observed were Ar₂⁺⁺, Kr₁₂⁺⁺, and Xe₇⁺⁺, the limit being the range of our mass spectrometer. The relative intensities of cluster ions Ar⁺ⁿ⁺ decrease exponentially with increasing n as noted in previous experiments on other solids, except for Ar₂⁺⁺ which shows a relatively smaller intensity. A more quantitative evaluation is difficult because the transmission of the quadrupole is uneven as a function of mass. Also, it should be noted that our energy filter mounted in front of the quadrupole mass spectrometer transmits only a relatively narrow 1-2 eV range of secondary ion energies. Since the secondary ion energy distribution is broader than that obtained with Ar⁺ as the primary ion, but the distribution of the secondary ion Ar⁺ is of comparable width in the two cases. With Xe⁺ as the primary ion, the maxima are not as clearly separated as was the case when Ar⁺ was the incoming projectile. The behavior of Kr⁺ as a primary ion is intermediate between Ar⁺ and Xe⁺. The kinetic energy distribution of doubly charged secondary ions is the same as that of the singly charged atomic ions.

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the only observed ion which contained more than a single krypton atom was Kr$_2^+$, and its intensity was only 5% of that of Kr$^+$.

Several of the measurements at 1:100, 1:200, and 1:500 matrix ratios were repeated with 3 keV and 1 keV He$^+$ primary ions. In keeping with the results obtained on pure rare gas solids, far fewer clusters were observed, particularly with 1 keV He$^+$ ions. In the latter case, Ar$^+$, Ar$^+$, Ar$^+$, Ar$^+$, ArK$^+$, and Kr$^+$ were the only peaks observed already at the 1:100 dilution.

Attempts to observe negative secondary cluster ions from the rare gas solids yielded only negative results.

Discussion

The present results confirm the previous claims$^{1,5,8}$ that SIMS measurements on molecular solids with very low heats of vaporization and very low sublimation temperatures are feasible. The most striking feature of the spectra is the abundance of rare gas cluster secondary ions formed with the heavier primary projectiles. This is not a serious limitation for matrix-isolation studies, since already with argon the cluster ion projectiles. This is not a serious limitation for matrix-isolation experiments, since already with argon the cluster ion projectiles. This is not a serious limitation for matrix-isolation studies, since already with argon the cluster ion projectiles. This is not a serious limitation for matrix-isolation studies, since already with argon the cluster ion projectiles. This is not a serious limitation for matrix-isolation studies, since already with argon the cluster ion projectiles. 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Disilver: Spectroscopy and Photoprocesses in Rare-Gas Matrices

Steven A. Mitchell, Geraldine A. Kenney-Wallace, and Geoffrey A. Ozin*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. Received November 25, 1980

Abstract: We report the absorption and fluorescence spectra of Ag₂ molecules in Ar, Kr, and Xe matrices at 12 K. A comparison is made with the absorption spectrum of Ag₂ in the gas phase, and detailed assignments of the matrix absorption bands are suggested. The absorption and fluorescence spectra are indicative of strong guest-host interactions involving the A₁Σ⁺ and C¼Π states of Ag₂ in rare-gas matrices. The emission spectrum produced by A→X Ag₂ excitation is interpreted in terms of an excited-state Ag₂ dissociation process, involving strong stabilization of the 3S + 1P Ag atomic fragments by matrix cage relaxation effects. Electronic relaxation of the C state of Ag₂ is discussed in terms of matrix cage relaxation, energy transfer to Ag atoms, and nonradiative decay to the A state.

Matrix isolation has proven to be a valuable technique for spectroscopic study of a wide variety of normally unstable metal complexes and molecular metal clusters. In particular, matrix trapping and stabilization of silver atoms and clusters have been extensively studied. We have recently shown that silver clusters can be formed in a highly controllable manner by photoinduced diffusion and aggregation of matrix-entrapped silver atoms. These studies have led to broader enquiries into the nature of electronic relaxation processes of matrix-isolated silver atoms and molecules, with a view to establishing guidelines for the possible extension of the photoinduced diffusion technique to other metal and matrix systems, and to investigate the photoprocesses of matrix-entrapped silver clusters generally. In a previous paper we reported the fluorescence excitation, emission, and polarization spectra of silver atoms isolated in Ar, Kr, and Xe matrices, and proposed a qualitative model for the excited-state interactions to account for the observed optical and photolytic properties. In this paper we extend these studies to include fluorescence spectroscopy and electronic relaxation of Ag₂ molecules in rare-gas matrices. The first matrix fluorescence spectrum of Ag₂ was reported by Kolb and Leutloff. We also present a more detailed analysis of our previously reported observations concerning photodissociation of matrix-entrapped Ag₂ molecules. Laser-induced fluorescence has been used to study the electronic spectra of a wide variety of matrix-isolated diatomic molecules, and to investigate the nature of the guest-host interactions. It is often found that the molecular constants are perturbed only slightly in the matrix environment, and in general quite weak guest-host interactions are indicated, although the matrix may influence the electronic relaxation behavior by inducing nonradiative transitions. However, it appears for the case of the excited states of Ag₂ that rather strong guest-host interactions are operative and that unusual electronic relaxation processes are induced by these matrix interactions.

Experimental Section

The experimental arrangement for matrix preparation and fluorescence studies has been described previously. Matrices were deposited in a highly controlled manner by photoinduced diffusion and aggregation of matrix-entrapped silver atoms. We have recently shown that silver clusters can be formed in a highly controllable manner by photoinduced diffusion and aggregation of matrix-entrapped silver atoms. The results obtained on krypton isolated in an argon matrix are highly encouraging. They suggest that even relatively poor matrix isolation ratios such as 1:100 to 1:1000 will be adequate for mass spectrometric investigations of matrix isolated species.

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Table I. Ag₂ Absorption Maxima in Ar, Kr, and Xe Matrices at 12 K

<table>
<thead>
<tr>
<th>λ, nm</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>261 (+720 cm⁻¹)</td>
<td>270</td>
<td>283</td>
<td>266</td>
</tr>
<tr>
<td>264 (+557 cm⁻¹)</td>
<td>275</td>
<td>289</td>
<td></td>
</tr>
<tr>
<td>273 (280)</td>
<td>296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>282 (290)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>389 390 391 435</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+2720 cm⁻¹)</td>
<td>[+2650 cm⁻¹]</td>
<td>[+2590 cm⁻¹]</td>
<td></td>
</tr>
</tbody>
</table>

* Absorption maxima due to secondary matrix sites appear in parentheses. The shifts of the major absorption bands from the (0,0) gas-phase transition energies are given in square brackets.

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