Photochemistry and spectroscopy of ions and other transient species in low temperature matrices

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Short Communication

Photochemistry and spectroscopy of ions and other transient species in low temperature matrices*

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Low temperature rare gas matrices provide a very useful environment for photochemical and spectroscopic studies [1, 2]. The low temperature solids, although chemically usually inert, often modify the photochemical behavior of the trapped species. The major mechanism by which this occurs is the "cage effect", which generally prevents the diffusion, particularly of larger molecules or fragments, from the trapping sites. As a result, unimolecular processes not requiring diffusion are enhanced with respect to bimolecular reactions or processes needing separation of reactive fragments.

Electrons can move relatively unhindered through the rare gas solids [3]. The photoionization of guest molecules by vacuum UV light therefore proceeds with a high quantum efficiency, while the competing photodissociation channels are suppressed and high concentrations of molecular or atomic ions can be produced cleanly by direct *in situ* photolysis with light of appropriate wavelengths. The ions generated in this way are then indefinitely stable in the 4 K sample and their spectroscopy and photophysics can be studied conveniently. We have generated close to 100 distinct molecular cations by this means in our laboratory in the last few years [4, 5] and we have investigated their properties by means of both absorption spectroscopy and time-resolved laser-induced fluorescence.

Ions are known to interact very strongly with rare gas matrices, with solvation energies of 1 - 2 eV. In spite of these strong interactions, meaningful spectroscopy of the ionic spectra can be performed provided that two conditions are fulfilled: (1) the interaction consists mainly in polarization of the solvent by the "point charge" and does not perturb the bonding in the guest appreciably; (2) the interaction is of similar magnitudes in the ground and excited electronic states, so that no significant phonon broadening of the spectra occurs. These are met satisfactorily for most ions in solid neon. The ionization potential of neon (21.559 eV) is much larger

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than the electron affinities of typical molecular ions (about 8 - 14 eV) and little chemical charge transfer interaction takes place there. The situation is often different in argon and in the heavier more polarizable rare gases. Since the 15.775 eV ionization potential of argon is much closer to the electron affinities of the guests, rather strong charge transfer interactions can take place. Such interactions will in general be state specific and usually stronger in the excited electronic state, whose electron affinity is greater by its excitation energy.

This can be exemplified by the diacetylene radical cation, which exhibits well-resolved and unperturbed spectra [6] in solid neon consisting predominantly of sharp zero-phonon lines. In solid argon, however, the emission is strongly red shifted and shows no vibrational structure. Only broad poorly resolved phonon wings exhibiting a strongly perturbed vibrational structure are seen in absorption. A comparison of the vibrational frequencies derived from the neon matrix spectrum with the gas phase results shows quite negligible (less than 0.2%) shifts in the vibrational intervals [6]. A similar lack of perturbation by the solid medium is found for CS_2^+ and for numerous other molecular cations. In fact, from the more than 100 distinct species that we have studied in the neon matrix, there are almost no instances of matrix shifts well outside the experimental accuracy.

A closer inspection leads to the surprising observation that for many species the gas—Ne matrix shifts are smaller for the cations than for the neutral parents. In cations the valence electrons are more tightly held by the excess positive charge on the nuclei, and this results in more compact electronic wavefunctions and less overlap with the solvent. An extreme example is provided by the comparison of the spectra of potassium atoms in solid argon [7] with those of the isoelectronic Ca^+ cation. While the potassium atomic emission exhibits an immense matrix red shift and the spectrum is several thousands of reciprocal centimeters broad, the Ca^+ spectrum is much sharper (about 200 cm^{-1}) and essentially unshifted from that of the gas phase.

An interesting group of ions for which studies of wavelength-, time- and polarization-resolved fluorescence provide a detailed insight is the halogenated benzene radical cations [8]. These species exhibit strong electronic spectra in the visible region, deriving from the $\tilde{B}$ $^2A_{2u} \rightarrow \tilde{X}$ $^2E_{1g}$ transition of the benzene radical cation. In the molecules retaining D_{6h} or D_{3h} symmetry and degenerate ground states, we observe very irregular emission spectra with a uniform polarization ratio $P = I_\parallel/I_\perp = 4/3$. A detailed analysis of the spectra yields very complete information about the Jahn—Teller distortion in these species. In cations of lower symmetry, e.g. 1,2,4,5-$C_6H_2F_4^+$, we see two distinct spectra. A harmonic array of emission bands exhibiting $P = 3.0$ is due to the $\tilde{B}$ $^2B_{3u} \rightarrow \tilde{X}$ $^2B_{2g}$ transition and characterizes the now non-degenerate ground state. A second considerably red-shifted band system which exhibits a predominant perpendicular polarization P of 0.5 is assigned to the $\tilde{B}$ $^2B_{3u} \rightarrow \tilde{A}$ $^2B_{1g}$ emission into the higher-lying component of the ground state split by asymmetric substitution.

In condensed phases, vibrational relaxation is typically very fast [9] and usually only emission from the vibrationless level is seen. However, because of the fully allowed nature of the $\tilde{B} \to \tilde{X}$ transition in fluorescence cations, a fluorescence from numerous excited vibrational levels of the $\tilde{B}$ state is observable [10]. Using selective excitation of individual vibronic levels of the $\tilde{B}$ state, followed by time-resolved detection of the fluorescence, we can gain, in addition to spectroscopic information, insight into the rates and mechanisms of vibrational relaxation and intramolecular energy redistribution in the $\tilde{B}$ state. By comparing studies carried out on numerous substituted benzene cations, we can draw several more general conclusions.

(1) The vibrational relaxation rates of single vibrational levels are in many cases surprisingly slow. They range from about 200 ps into the sub-picosecond range.

(2) There is a general but not monotonic increase in relaxation rates with vibrational energy.

(3) The intramolecular energy randomization and redistribution is slow compared with the overall rate of vibrational relaxation.

(4) The relaxation rates are strongly affected by the molecular symmetry. The D_{6h} $C_6F_6^+$ cation shows the slowest relaxation, and also the D_{3h} species $C_6H_3F_3^+$ and $C_6H_3Cl_3^+$ relax rather slowly. The fastest relaxation is exhibited by the $asym$-$C_6H_3F_3^+$ of C_s symmetry, where only the emission from the lowest excited $\tilde{B}$ state level with an estimated lifetime of about 5 ps was detected. The C_{2v} or D_{2h} species (*e.g.* $C_6HF_5^+$ or $C_6H_2F_4^+$) show intermediate relaxation.

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