

Mass Selected Ions in Solid Neon: Matrix Damage and Site Effects

Vladimir E. Bondybey and Martin Lorenz

*Institut für Physikalische und Theoretische Chemie
Technische Universität München, Lichtenbergstraße 4
85748 Garching, Germany*

The problems and advantages of mass-selected ion deposition in matrices are briefly reviewed and discussed, and initial results with our new apparatus are reported. Both laser induced fluorescence, visible and infrared absorption spectra of ions are detected. Using samples with natural abundance, we demonstrate that individual isotopomers of CS_2^+ can be separately deposited and their spectra analyzed. Our studies with halogenated benzene radical cations indicate that deposition from the energetic beam results in matrix damage which in turn leads to site effects and inhomogeneous broadening. The perturbed sites of lower symmetry have a considerable effect on the guest spectroscopy, leading to spectral shifts and change in the spectroscopic selection rules.

1. INTRODUCTION

When the matrix isolation method was originally developed, its major goals were studies of free radicals and other unstable molecules and neutral transient species.¹ Studies of ions were for several reasons at the time not seriously contemplated. In the first place, it was widely believed that the weakly bound matrix could not withstand the strong Coulombic forces between ionic species, in the second place, one also thought that even if ions were prepared, their spectra would be extensively perturbed by the strong interaction with the host solid. The earliest experimental observations of ionic spectra in matrices were therefore basically accidental, and when observed, the carriers were in fact first assigned to neutral species.

McCarty and Robinson have already in 1959 observed a strong absorption spectrum in the visible, which they assigned to the $a^3\Pi_u$ - $d^3\Pi_g$ Swan

bands of diatomic C_2^- , a surprising assignment since the lower state of this transition is known not to be the ground state. The same bands were subsequently observed by at least three other groups in some ten different works, and it was speculated that either the lower state has an extremely long lifetime, or that the ordering of the states is changed by the solid matrix. The solution to the mystery was finally found a decade later by Milligan and Jacox^{3,4}, who noted that the molecular constants more closely resemble those of the Herzberg-Lagerqvist bands of the C_2^- ion⁵, than of the neutral C_2 . Final confirmation of this suggestion then came from the work of Frosch, who observed emission from both the Herzberg-Lagerqvist bands of C_2^- and the Swan bands of C_2 in matrices containing acetylene under X-Ray irradiation.⁶ Finally, observation of laser induced fluorescence of C_2^- confirmed that the lower state indeed is the ground state.⁷

Similarly misinterpreted were the earliest infrared observation of free matrix isolated ions. Strong absorptions observed by Pimentel and coworkers at 696.4 and 727.4 cm^{-1} in experiments designed to generate the hydrogen dihalide radicals were assigned to HCl_2 and HBr_2 ,^{8,9} respectively, but the proximity of these frequencies to those of the well known dihalide anions HCl_2^- and HBr_2^- was noted. An additional band detected at 905 cm^{-1} in solid argon was independent of the halogen, but shifted to 645 cm^{-1} in deuterated samples. This band, apparently due to a single hydrogen atom, shifted significantly to 852 (and 607 cm^{-1}) when krypton was used instead of argon. It was also noted that all bands could be consistently interpreted by assigning dihalide absorptions to the anions, rather than the neutral radicals, and the halogen independent frequencies to the HAr_2^+ and HKr_2^+ cations, which are isoelectronic with the dihalide anions. But in the end, the neutral assignment of all the absorptions was preferred since the spectra appeared also under conditions where production of ions seemed energetically impossible.

Subsequently the same absorptions have been observed in numerous other studies, and "reassigned" to the ions often without much additional experimental evidence. Further studies of ions in matrices have solved the mystery of the ion production, and revealed that several effects combine to make ion production and stabilization in matrices easier.¹⁰ In the first place, the solvation by the matrix stabilizes substantially ionic species, so that the ionization potentials can be lowered by as much as 2 eV. In the second place, in the solid matrix the ions are not necessarily produced at an "infinite" distance, so that one gets the further benefit of stabilization by the screened Coulombic potential. There is now little disagreement, that the ionic interpretation is correct, and in fact the HAr_2^+ and HKr_2^+ species are forerunners of a series of strongly ionic rare gas compounds recently observed

by Räsänen and coworkers.^{11,12}

In the first matrix studies of molecular ions, several methods were employed for their production. In the first place, the ions can be produced in the gas phase, for instance by discharge,¹³ or more recently by laser vaporization,^{14,15} and deposited and frozen together with a large excess of inert carrier gas in the solid matrix. A very convenient alternative is preparation of the ions in situ, for instance by X-Rays, electron bombardment, or vacuum UV photolysis. In particular neon matrices are transparent at wavelengths ($E_{gap} = 21.69$ eV), at which numerous organic or inorganic molecules can be ionized, and subsequently spectroscopically investigated. The latter technique is particularly successful if the ions have stable excited electronic states and one can employ sensitive laser induced fluorescence (LIF) for their detection. In this way excellent quality spectra of a wide range of organic species could be recorded and analyzed.

It is usually difficult to accumulate in this way ionic concentrations adequate for observation by conventional spectroscopy. For this purpose a technique was developed, where the matrix itself acts as a planar waveguide.¹⁶ The light injected "sideways" into the matrix propagates, confined by the reflections on the substrate metal mirror on one side, and by a total internal reflection on the rare gas-vacuum interface on the other, and one gets the benefit of long absorption pathway. Unfortunately, the in situ photolysis in general only works for "parent" ions, and is more difficult to apply to ionic fragments.

While depositing species from various discharges, one usually gets a complex mixture of neutral and ionic fragments, and their reliable identification may often be a nontrivial problem. An obvious alternative obviating this problem would seem to be mass selection of the ions in the gas phase prior to deposition. There are, however, numerous difficulties associated with this seemingly simple project. In the first place, it is difficult to slow down the ions below some 10-20 eV. An ion reaching the surface of for instance solid neon with an energy of > 10 eV can easily fragment. It can also "melt" some 3000 matrix atoms, or cause the evaporation of about 500, which in turn can lead to enhanced diffusion. The incoming ion can penetrate deep into the solid, resulting in aggregation and reactions with other species already present in the matrix. In spite of the inherent difficulties, several groups have reported successful deposition of mass selected ions and observations of their spectra,¹⁷⁻²⁴ and in particular the trailblazing experiments of Maier and his group²⁵⁻²⁷ have demonstrated that the problems can be solved.

We have now constructed an apparatus for mass selected ion deposition in our laboratory, which is in many respect similar to the successful design

of Maier and coworkers. The subject of the present talk will be some interesting results and insights obtained in the first experiments using the new apparatus.

2. EXPERIMENTAL

As noted above, the apparatus constructed in our laboratory has features similar to that of the Maier group, and it is described in detail in a previous publication.²⁸ The ion source in our experiment consists simply of a 12 mm Swagelok T piece. The precursor gas flows through the collinear sections and 50 W of 2.45 GHz microwave power are applied to a needle electrode located in the perpendicular arm. The pressure in the source chamber evacuated by a 360 l/s turbo-molecular pump is 10^{-4} - 10^{-2} mbar. To improve the confinement of the charged species produced in the discharge, we use the magnetic field from a ring shape magnet surrounding the Swagelok. The source is typically held at +20 V, and the discharge products pass through a grid and are accelerated towards a 2 mm skimmer held at -20 V. Since both cw experiments, as well as experiments with a pulsed laser vaporization source were foreseen in our apparatus, we have opted for a quadrupole mass filter which, unlike for instance TOF, allows both modes of operation.

The ions produced in the source pass through a skimmer, are focused using an einzel lense and deflected 90° in a quadrupole electric field. Depending on polarity, the ionic species are either deflected towards a Faraday cup, permitting to measure the total source ion current, or in the opposite direction, to be focused by a second lense, L2, onto the entrance aperture of the quadrupole mass filter. The neutrals jet remains undeflected and is pumped by a second 360 l/s turbo-molecular pump.

The mass selection is accomplished with a modified commercial triple stage HIDEN HAL/3F quadrupole filter with 12 mm rods, which has a specified mass range of up to 500 amu, and a better than unit mass resolution throughout this range. There is a trade-off between resolution and transmission which is 10%, but can be made higher by sacrificing resolution. The quadrupole mass filter was fitted with 7 mm entrance and exit apertures, and is differentially pumped by a 150 l/s pump.

Following mass selection, the ion beam is directed towards the matrix substrate by means of a further einzel-lens L3. The substrate, a silver coated copper plate, is cooled by a LEYBOLD RDG 580 closed-cycle refrigerator to 7-8 K. The ion beam is deposited on the substrate simultaneously with the matrix gas, neon in the present case. In order to maintain the overall neu-

trality of the matrix, and avoid building up space charges and stray fields, the matrix was sprayed by electrons from a hot tungsten filament held at negative potentials of up to $U_{Fila} = -200$ V. We experimented with alternating the ion and electron deposition, but in the end continuous operation proved to be most efficient, with optimal results being obtained with the electron current being maintained at about five times the ion current.

The process of ion deposition is shown schematically in Fig. 1. The non-conducting matrix surface is irradiated by electrons from the filament and it is charged negative until the surface reaches the same potential as of the filament. Additional electrons are now deflected by the negative potential of this space charge zone — an equilibrium has been reached. Arriving ions, which have an initial kinetic energy of $E_i = 20$ eV, are accelerated towards the matrix and hit the surface with the final energy $E_f = E_i + e|U_{Fila}| = 220$ eV. In this way, the voltage of the neutralizing filament has important influence on the damage done to the matrix by the impact of the ion beam which will be discussed in detail in the next section.

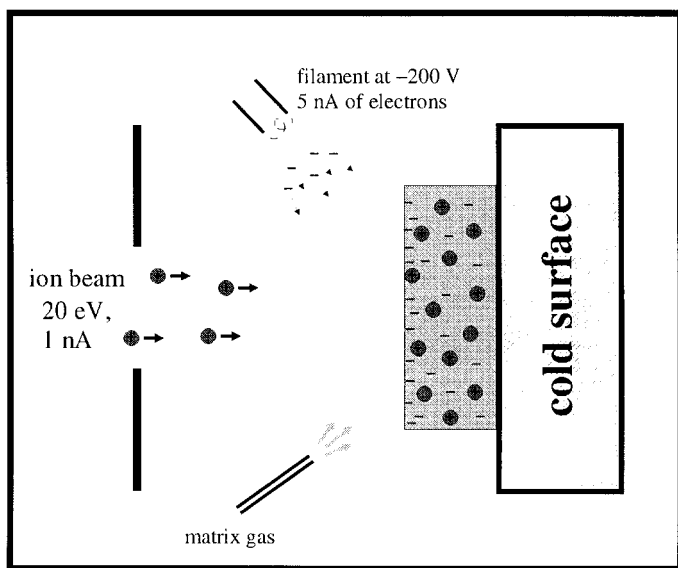


Fig. 1. The process of ion deposition: The mass-selected ions with kinetic energy of 20 eV are codeposited with electrons and excess matrix gas. The electrical neutrality of the matrix is maintained in an equilibrium process and occasionally, some ions may be neutralized.

In order to optimize the experiment, the ability to measure the ion current is essential. For this purpose, one Faraday cup permitting measurement of the total ion current is located in the deflection chamber. A second detector close to the cold surface allows measuring the mass selected ion current reaching the sample. The weak currents are amplified by a FEMTO DLPCA 100 current amplifier and digitized in the quadrupole control unit. Currents as low as 100 fA can be easily detected and we obtain mass spectra with S/N better than 10000:1. With the mass filter set to the desired mass, all the experimental parameters can be adjusted for the maximum current. With our microwave discharge source we could produce for both CS_2^+ and C_6F_6^+ mass-selected currents of up to 2 nA.

After deposition, the matrix the matrices are characterized spectroscopically using a BRUKER IFS 120 HR Fourier transform spectrometer, equipped with beam-splitters and detectors for the 500 - 30000 cm^{-1} spectral range. IR absorption spectra are measured using a liquid nitrogen cooled MCT (mercury-cadmium telluride) detector at a resolution of 0.06 cm^{-1} , whereas all other spectra were recorded with 0.5 cm^{-1} resolution. Laser excitation spectra are obtained with the help of an Ar^+ laser pumped power stabilized dye laser operating with a stilbene-3 dye. The total emission of the sample is detected using a PMT (and appropriate optical filters) connected to a lock-in amplifier. Laser induced fluorescence spectra are measured with the FT spectrometer using the same detector, typically at a resolution of 0.5 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. Deposition and Spectra of Mass Selected CS_2^+ Isotopomers

The carbon disulfide cation was selected for the initial studies because it was previously studied,²⁹⁻³¹ and it is known to give relatively simple, sharp and well resolved electronic spectra in solid neon matrices. After some optimization, our source yielded a stable current of up to 2 nA at the mass of the $^{12}\text{C}^{32}\text{S}_2^+$ cation, 76 AMU. Besides this parent ion, which was the strongest mass peak, and its isotopic varieties, also the easily identifiable CS^+ and S^+ and C^+ fragments, as well as S_2^+ appeared in the mass spectrum.

The laser excitation spectrum of a sample resulting from about three hours deposition of 1.5 nA of the 76 AMU ion current shows clearly the known $\text{A } ^2\Pi_u \leftrightarrow \text{X } ^2\Pi_g$ transition of the CS_2^+ ions with origin at 21010.57 cm^{-1} . While this proves that the ions are present in the matrix, it leaves open the possibility that these are not due to the mass selected beam, but to neutral CS_2 leaking in spite of three stages of differential pumping from the

ion source into the cryostat, and being ionized in situ in the matrix by the electron beam. To answer unambiguously this question, we have carried out a separate experiment, depositing again for three hours a 0.15 nA current of mass 78 AMU instead of mass 76. In this case the origin band is distinctly shifted to 21011.05 cm^{-1} , and also all the bands due to the higher vibrational levels of the excited $A^2\Pi_u$ state exhibit shifts appropriate for the $^{34}\text{S}^{12}\text{C}^{32}\text{S}_2^+$ isotopic cation, establishing clearly that the ions are not being formed in situ, but are deposited from the mass selected beam. It also demonstrates the ability to produce useful spectra by depositing minor isotopic species from samples with natural isotopic abundance.

3.2. Vibrational Structure of CS_2^+ and Negative Anharmonicity of the ν_3 Vibration

The absorption and resolved emission spectra of CS_2 are quite similar, reflecting similarities in the vibrational structures of the two states involved. Both of them are characterized by strong "Fermi resonances" between the symmetric stretching vibration ν_1 , and even overtones of the bend, resulting in the appearance of progressions in so called "Fermi polyads". Besides these resonant groups of bands, also even overtones of the third fundamental, $2\nu_3$ and $4\nu_3$ appear in the emission spectrum at 18592.80 and 16170.30 cm with appreciable intensity, reflecting the large change in the ν_3 vibrational frequency between the ground and excited electronic states. From the frequencies of $2\nu_3'' = 2417.80$ and $4\nu_3'' = 4840.30 \text{ cm}^{-1}$ one can deduce the molecular constant values of $\omega_3'' = 1207.14$ and $x_{33} = -0.5875$. The asymmetric potential displays negative anharmonicity, that is the level spacing increases with the value of the vibrational quantum number v . This is usually attributed to the presence of a quartic term in the potential energy expression, and one treats the energy levels in terms of either a harmonic oscillator with a perturbing quartic term, or more commonly as a mixed harmonic-quartic oscillator, where the constant a changes from 0 to 1 as one goes from a pure harmonic to a pure quartic oscillator

$$H_m = P^2 + (1 - a)Q^2 + a^{2/3}Q^4 \quad (1)$$

By setting up the P and Q matrices in a harmonic oscillator basis set, one gets from the observed $2\nu_3''$ and $4\nu_3''$ levels the constant $a = 0.004724$. In either case, either using the Morse oscillator, or mixed harmonic-quartic oscillator one can compute an almost identical value of the vibrational frequency $\nu_3 = 1208.31 \text{ cm}^{-1}$. Examination of the infrared absorption spectrum in this region reveals a weak, sharp band fairly close to the computed frequency, at 1206.92 cm^{-1} , which disappears upon annealing of the sample.

3.3. Jahn-Teller Effect in the Benzene Cation and its Symmetrically Substituted Homologues

Halogenated benzenes represent another group of compounds whose radical cations have been extensively studied by matrix spectroscopy.^{32,33} Simple Hückel Molecular Orbital theory shows that the unhybridized p electrons on the six carbon atoms of the benzene ground state occupy an a_{2u} and a doubly degenerate e_{1g} binding molecular orbital, yielding a stable, closed shell structure. In the cation one of the electrons from the highest occupied e_{1g} molecular orbital (HOMO) is missing, resulting in a doubly degenerate $X\ ^2E_{1g}$ ground state. A $\pi - \pi$ promotion of one of the a_{2u} electrons into the e_{1g} orbital yields a low exciting $B\ ^2A_{2u}$ electronic state, and represents the lowest energy fully allowed electronic transition of the cation. In benzene itself another electronic state resulting from promotion of one of the σ electrons lies below the $^2A_{2u}$ state, and provides a "gateway state" for its non-radiative relaxation, that is its interaction results in severe broadening of the B state and shortening of its lifetime. When, however, at least 2-3 hydrogen atoms on the benzene ring are substituted by halogens, the energy needed for the $\pi - \pi$ relative to the $\sigma - \pi$ excitation is lowered to the extent that the $B\ ^2A_{2u}$ state becomes the lowest excited electronic state. The pathway for its non-radiative relaxation is closed, the spectra become sharp, and the radical cations fluoresce with near unity quantum efficiency, and can thus be conveniently investigated by laser induced fluorescence.

As we explained in previous publications^{33,34}, the excitation spectrum shows clearly the distortion of the ion due to Jahn-Teller effect. While in a symmetry allowed transition of a molecule with a D_{6h} symmetry only the a_1 modes ν_1 and ν_2 should appear, most prominent in the spectrum are actually vibrations ν_{18} , ν_{17} , ν_{16} , and ν_{15} - precisely the modes of e_{2g} symmetry which according to theory should become active, if the ground state symmetry is lowered from D_{6h} to D_{2h} . The presence of Jahn-Teller effect is then confirmed by analysis of the resolved emission spectra, which unlike the absorption spectra appear quite irregular and erratic - they reflect the vibrational structure of the degenerate ground state distorted by the Jahn-Teller effect.

3.4. Spectrum and Concentration of sym-Trifluorobenzene Radical Cation

Absorption spectra of a sample resulting from a codeposition of ≈ 1 nA current of a mass 132 AMU beam with pure neon shows clearly the known visible absorption of the $1,3,5\text{-C}_6\text{H}_3\text{F}_3^+$ radical cation. The strongest 0-0

origin band located at 21769.6 cm^{-1} exhibited an integrated absorbance of 0.094 cm^{-1} , and it was followed to higher energies by weaker vibrational structure. While numerous molecular ions were previously studied, relatively little is known about the achievable ion concentration. In the case of mass selected beam deposition, the extent to which the gas phase ions actually reach the sample, and survive the recombination, fragmentation and other reaction which can occur in the matrix or on its surface is therefore of considerable interest.

In the present experiments, there are in fact two independent ways in which one can estimate the ion concentration, or at least establish its limits. In the first place, by knowing the ion current reaching the matrix and the deposition time, one can easily compute the number of moles of the sample, and compare it with the number of moles of the simultaneously deposited matrix gas. This easy computation in the experiment with the $1,3,5\text{-C}_6\text{H}_3\text{F}_3^+$ gives a molar concentration of about $0.9\text{-}1\times 10^{-9}$, that is one part per billion, provided no ion-electron recombination, or other reactions destroying the ions take place. Very similar numbers were in this way also obtained for the other molecular ions studied in this work.

There is, however, a second, independent way, in which the ion concentration can be estimated. The fully allowed B-X transition in the $1,3,5\text{-C}_6\text{H}_3\text{F}_3^+$ cation is known to have in the matrix a lifetime of about 50 ns. This value exhibits little dependence on temperature, does not change appreciably when the molecule is deuterated, and is only slightly shorter than the gas phase lifetime. It is therefore very likely that non-radiative processes are insignificant, and the lifetime is basically radiative. Under this assumption, one use the integrated absorbance from the obtained spectra to compute the ion column density, and obtain again from the known thickness of the matrix the ion concentration. While again the uncertainties in a number of the values entering the computation are relatively high, one obtains cation concentrations of the order of $1\text{-}3\times 10^{-10}$. Comparison of the numbers obtained in the two independent ways suggests, that at least 10-20 % of the ions survive the deposition process. Consistent with this assessment, that recombination should not be dominant, while we could observe weakly the absorption of the CS_2^+ cation, the absorptions which could be attributed to either neutral CS_2 or to the CS fragment were apparently too weak for detection.

3.5. Matrix Damage and Multiple Sites in the $\text{C}_6\text{F}_6^+ \text{B}^2\text{A}_{2u} \leftrightarrow \text{X}^2\text{E}_{1g}$ Spectroscopy

Laser excitation spectra of two different samples, each resulting from 3 h deposition of a beam current of ≈ 1 nA at mass 186 amu, are shown in Fig. 2. The difference between the two is in the energy of the ions impinging upon the matrix, which is estimated to be 220 eV for the top spectrum but considerably lower (20 eV) for the bottom one. While the bottom spectrum resembles the spectrum reported in a previous study³³ where the ions were generated by in situ vacuum UV ionization of neutral hexafluorobenzene, in the top spectrum where the ions were deposited with higher kinetic energy, each of the strong vibronic bands of hexafluorobenzene seems to be replaced by a group of several bands. Clearly, while in the sample where the beam was deposited with lower energy, as well as in the photo-ionized sample there is one dominant site, denoted by A, in the sample deposited with higher energy there are several "sites", that is the cations occur in the neon matrix in several different local environments. The most intense subsidiary sites are denoted by the letters B and C, and can be seen to occur, albeit weakly, also in the bottom spectrum.

The fact that the origin of the additional bands is inhomogeneous, is confirmed by examining the emission spectra: exciting the B and C bands, which are blue shifted by 16 and 33 cm^{-1} , respectively with respect to the A bands, results in fluorescence whose origin is shifted by the same amount. The presence of several similar "spectra" shifted by similar amounts both in emission and excitation spectrum is a characteristic symptom of several distinct sites, that is in the present case the A, B and C bands correspond to the C_6F_6^+ cations "perturbed" by a slightly different local environment. The almost complete absence of the multiple sites from the spectra produced by "in situ" ionization, and their presence, and dependence of ion energy in the case of ions deposited from the gas phase suggests that they are the result of matrix damage due to the ion bombardment.

Some time ago we have noted that also in the case of matrix isolated linear carbon chain ions of the type $\text{X-C}_n\text{-Y}^+$ (where X and Y can be for instance H or CN), there exists a considerable difference between the spectra of ions produced in situ, and of the same ions deposited from a mass selected ion beam. While in situ study in our laboratory yielded very sharp bands, the ion beam deposited samples by Maier et al. gave usually bands with more than 100 cm^{-1} widths.³⁵ We have previously suggested³⁶ that this difference is probably due to matrix damage, and the present results, observing an analogous effect for quite different type of ions clearly provides support for this point of view.

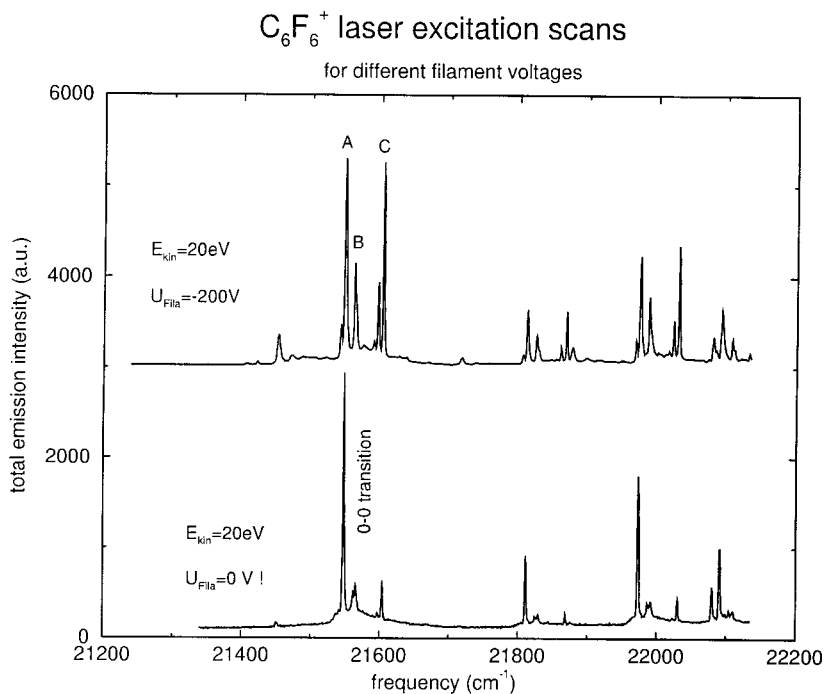


Fig. 2. $C_6F_6^+$ laser excitation spectra for different kinetic energies: 220 eV (top trace) and 20 eV (bottom trace).

3.6. Local Site Symmetry and Spectroscopic Selection Rules

Interesting insights can be gained by comparing the spectra of the ions in different sites. Ordinarily, such spectra appear to be almost identical except of a uniform shift of all the bands, corresponding to slight differential shifts in the energies of the electronic states involved in the transition. Also in the present case of $C_6F_6^+$, the absorption-laser excitation spectra show just such an effect, the resolved fluorescence, however, exhibits besides the usual uniform shift of all bands, additional changes in the spectrum, reflecting changes in the vibrational structure of the $X\ ^2E_{1g}$ ground state. As noted previously, the structure of this state is distorted due to the Jahn Teller effect, and while the excitation spectrum, reflecting the structure of the upper $B\ ^2A_{2u}$ electronic state consists of regular arrays involving several nearly harmonic vibrational frequencies, the emission spectrum lacks this

regularity, with only a progression in the totally symmetric a_{1g} mode ν_2 , the "ring breathing" frequency, being clearly recognizable.

The bands of this progression are observable at least to $\nu_2=2$, and they are shown for the main site A in Fig. 3, and compared with the corresponding sections of the spectra in the subsidiary sites B and C in the lower panels, whose frequency scales have for clarity been shifted in frequency by 12.9 and 55.3 cm^{-1} , so that the 0-0 bands overlap. One can clearly see that while for the main site a single sharp band is observed for each value of ν_2 , in the panels B and C each band has a broader satellite shifted ≈ 34 and ≈ 45 cm^{-1} , respectively, towards lower energies. This suggests the presence of a very low lying level above the vibrational level of the ground state as well as above each excited ν_2 level. These energies are way too low to correspond to an intramolecular vibrational mode of the ion, and surely too high to correspond to its rotation. While, in principle, the possibility that this mode could correspond to a "translational" mode of the ion, it is significant that similarly shifted satellites are not observed for the other, non-totally symmetric vibrational levels.

As noted above, the ground state of the cation, X^2E_{1g} , is a doublet state, whose spin orbit splitting is unknown. While a few theoretical works discussing this problem predicted a smaller splitting between the fine structure components, the observed value is of the same order of magnitude as, for instance, the fine structure constant $A_v = 77.12 - 0.655v + 0.0057v^2$ (in cm^{-1}) observed in the $X^2\Pi$ ground state of diatomic CF.³⁷ This raises the possibility that the extra level detected in the subsidiary sites is due to the higher spin orbit component of the ground state. Here again two possibilities have to be considered. Either is the forbidden transition in the main site A too weak to be observed, but becomes allowed in the "perturbed" sites B and C, or is the splitting in the main site too small to be resolved, but the near degeneracy is split in these sites. In either case, the spin-orbit splitting interpretation is consistent with the broader appearance of the satellite bands. In almost every case where spin-orbit splitting in multiplet states in matrices was observed, the higher level was broadened as a result of fast non-radiative relaxation into phonon states built upon the the levels of the lower spin orbit component.

In either case, the most likely cause of this difference between the "main" and "subsidiary" sites is the local geometry and symmetry, and it is of interest to consider from this point of view the likely nature of the trapping site. The lowest energy structure of rare gas solids is experimentally known to be FCC, but neutron scattering studies have suggested that gas phase deposited sample contain both FCC and HCP regions, with the presence of impurities favoring the growth of the HCP abundance. In either case,

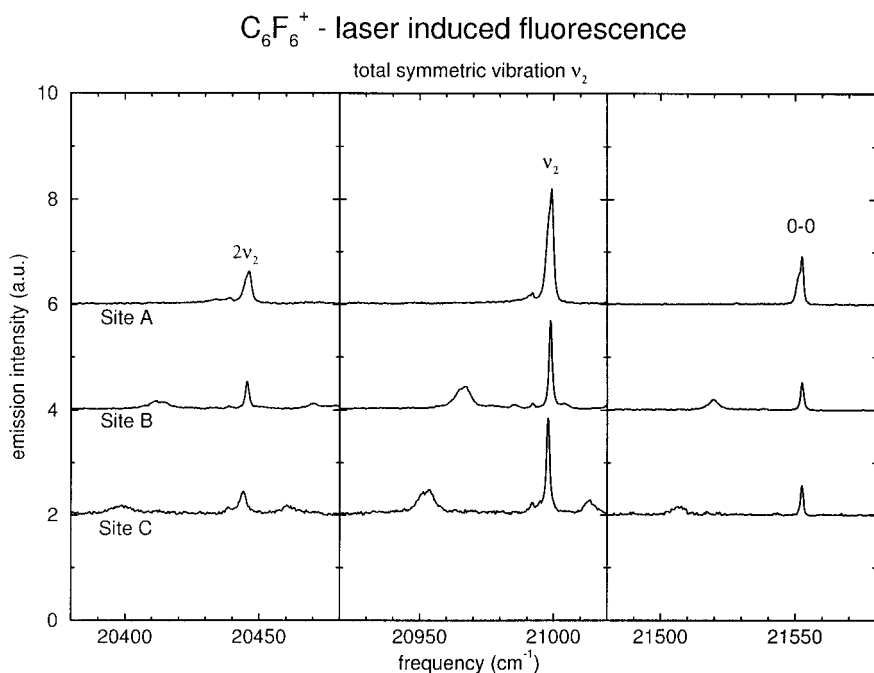


Fig. 3. LIF of C_6F_6^+ showing the total symmetric vibration ν_2 in the doubly degenerated electronic groundstate X^2E_{1g} .

the structure consists of identical planes with hexagonally arranged rare gas atoms, with the difference between the HCP and FCC structures being only in the arrangement of these planes. Considering the nearest neighbor distance between two neon atoms, and the geometry of the C_6F_6 molecule, it appears that the most natural way to accommodate the guest is to replace seven neon atoms in one of these planes, as shown in Fig. 4, yielding in each case a site of relatively high symmetry. The site will exhibit in an HCP lattice a hexagonal D_{3h} local symmetry, while in the case of FCC it will be S_3 three-fold improper rotation axis, with a center of inversion.

In the case of the in situ produced ions, the geometry of the site is unlikely to change during the photoionization process. We suggest that the symmetry in the subsidiary sites, resulting from the deposition of the energetic ions from the ion beam is lowered as a consequence of the damage. The exact nature of the site is unknown, but it may simply be an additional vacancy, that is an additional matrix atom missing in the immediate neigh-

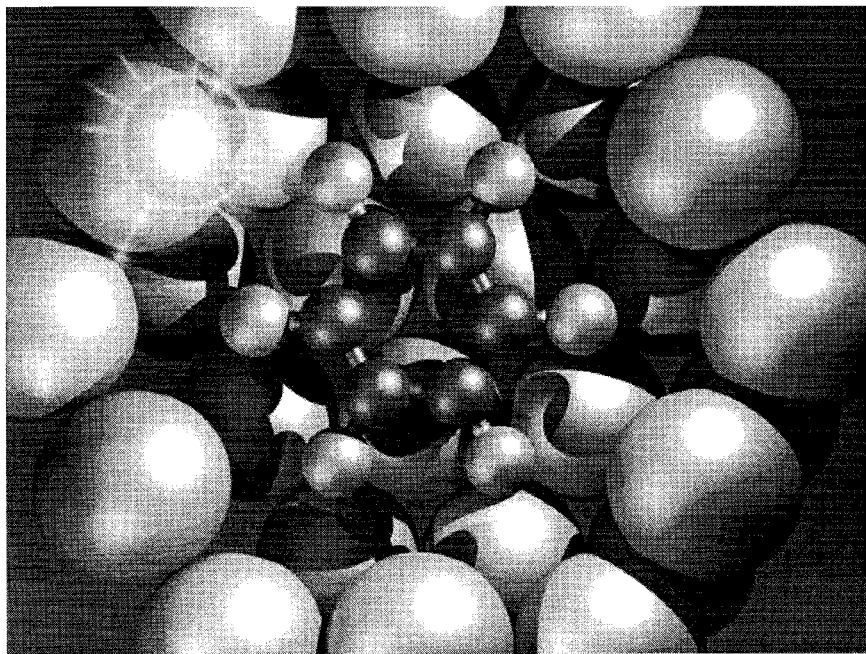


Fig. 4. The C_6F_6^+ cation embedded in a neon matrix.

borhood of the isolated ion. The lowered symmetry has little effect upon the intramolecular vibration - the values of the ν_2 vibrational frequencies and their overtones are to within about 1 cm^{-1} identical in all the three sites, but it appears to affect the selection rules, and also influences the spin orbit splitting between the $1/2$ and $3/2$ components, since comparison of the B and C sites yields considerably different values of ≈ 33 and 45 cm^{-1} , respectively.

3.7. Effect of Sites on the Jahn-Teller Distortion

As noted in the above section, the frequencies of the totally symmetric ν_2 mode, and of its overtones are basically unaffected by the changes in the trapping site and its symmetry. Quite different is the behavior of the Jahn-Teller active e_{2g} vibrational modes, as is exemplified by Fig. 5. Here the top panel shows sections of the fluorescence spectrum of C_6F_6^+ in the main "unperturbed" site A. As shown in the right hand section, easily identifiable

in emission are the lowest frequency e_{2g} modes $\nu_{18} = 288.8 \text{ cm}^{-1}$, $\nu_{17} = 417.2 \text{ cm}^{-1}$, with several bands previously shown to be due to their combinations and overtones being present at higher energies. An identical pattern of bands is then repeated built upon the totally symmetric ν_2 level, as well as upon its overtones, as shown in the two spectral sections further towards the left.

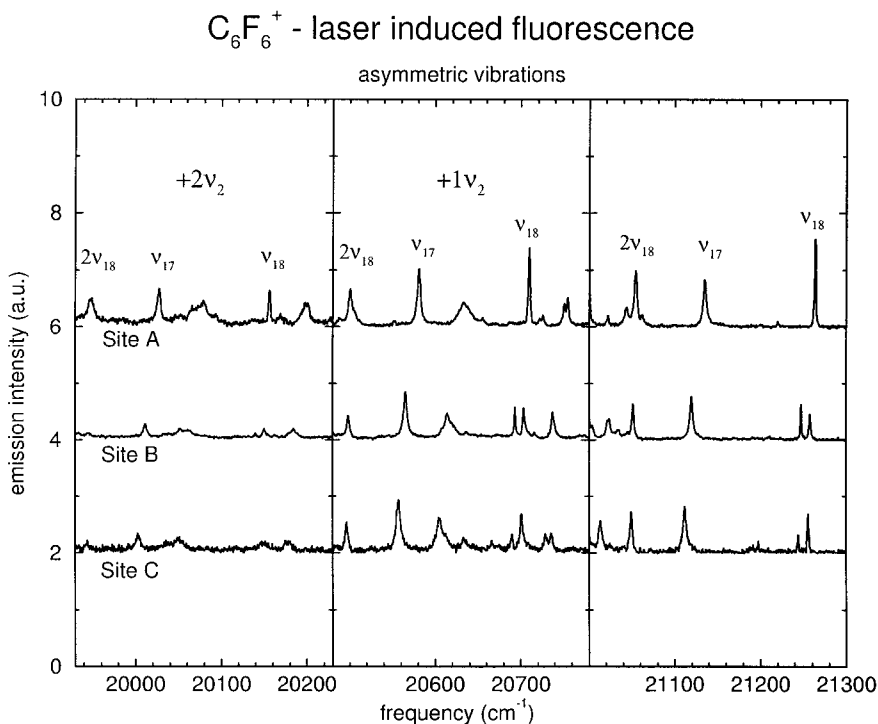


Fig. 5. LIF of C_6F_6^+ showing the Jahn-Teller active modes ν_{17} and ν_{18} in combination with ν_2

The bottom two spectra then show the corresponding sections of the spectra in the perturbed subsidiary sites B and C, which have again been shifted by the appropriate amounts needed to make the 0-0 origin bands of all the sites coincide, to make more apparent the changes in the vibrational structure. It is immediately visible that in the place of the ν_{18} level now appear two bands, both of them shifted to higher energies compared with the main site frequency. The two bands are at 294.7 and 305.0 cm^{-1} in the

site B and 296.9 and 308.3 cm^{-1} in site C. Similarly also the ν_{17} mode is blue shifted from its 417.2 cm^{-1} frequency in the main site to 432.8 and 440.9 cm^{-1} in the B and C sites, respectively. The same spectrally shifted band patterns are again repeated in combination with ν_2 and $2\nu_2$, as clearly visible in the Figure.

In previous studies of halogenated benzene radical cations it was already noted that while the ground state structures in neon matrix are very similar to the structure observed in the gas phase, the shifts and perturbations of the Jahn-Teller active modes and levels were distinctly larger than those of the levels not involved in the distortion, as in the present case of the totally symmetric $a_g \nu_2$. The present study of the effect of sites gives additional evidence demonstrating this sensitivity of the Jahn Teller distortion to local environment and its symmetry.

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REFERENCES

1. E. Whittle, D. A. Dows, and G. C. Pimentel, *J. Chem. Phys.* **22**, 1943 (1954).
2. M. McCarty and G. W. Robinson, *J. Chim. Phys.* **56**, 723 (1959).
3. D. E. Milligan, M. E. Jacox, and L. Abouaf-Marguin, *J. Chem. Phys.* **46**, 4562 (1967).
4. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **51**, 1952 (1969).
5. G. Herzberg and A. Lagerqvist, *Can. J. Phys.* **46**, 2363 (1968).
6. R. P. Frosch, *J. Chem. Phys.* **54**, 2660 (1971).
7. V. Bondybey and J. W. Nibler, *J. Chem. Phys.* **56**, 4719 (1972).
8. V. E. Bondybey, G. C. Pimentel, and P. N. Noble, *J. Chem. Phys.* **55**, 540 (1971).
9. V. E. Bondybey and G. C. Pimentel, *J. Chem. Phys.* **56**, 3832 (1972).
10. L. E. Brus and V. E. Bondybey, *J. Chem. Phys.* **63**, 3123 (1975).
11. M. Pettersson and M. Räsänen, *J. Chem. Phys.* **102**, 6423 (1995).
12. M. Pettersson, J. Lundell, and M. Räsänen, *Eur. J. Inorg. Chem.* **729** (1999).
13. A. Thoma, B. E. Wurfel, R. Schlachta, G. M. Lask, and V. E. Bondybey, *J. Phys. Chem.* **96**, 7231 (1992).
14. T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.* **74**, 6511 (1981).
15. V. E. Bondybey and J. H. English, *J. Chem. Phys.* **74**, 6978 (1981).

16. V. E. Bondybey, T. A. Miller, and J. H. English, *J. Chem. Phys.* **72**, 2193 (1980).
17. S. Fedrigo, F. Meyer, D. M. Lindsay, J. Ligniers, J. C. Rivoal, and D. Kreisler, *J. Chem. Phys.* **93**, 8535 (1990).
18. S. Fedrigo, W. Harbich, and J. Buttet, *J. Chem. Phys.* **99**, 5712 (1993).
19. Z. Hu, B. Shen, Q. Zhou, S. Deosaran, J. R. Lombardi, D. M. Lindsay, and W. Harbich, *J. Chem. Phys.* **95**, 2206 (1991).
20. Z. Hu, J.-G. Dong, J. R. Lombardi, and D. M. Lindsay, *J. Chem. Phys.* **97**, 8811 (1992).
21. M. S. Sabo, J. Allison, J. R. Gilbert, and G. E. Leroi, *Appl. Spectrosc.* **45**, 535 (1991).
22. T. M. Halasinski, J. T. Godbout, J. Allison, and G. E. Leroi, *J. Phys. Chem.* **98**, 3930 (1994).
23. S. Fedrigo, T. L. Haslett, and M. Moskovits, *J. Am. Chem. Soc.* **118**, 5083 (1996).
24. T. L. Haslett, K. A. Bosnick, and M. Moskovits, *J. Chem. Phys.* **108**, 3453 (1998).
25. D. Forney, M. Jakobi, and J. P. Maier, *J. Chem. Phys.* **90**, 600 (1989).
26. J. P. Maier, *Mass Spectrom. Rev.* **11**, 119 (1992).
27. J. P. Maier, *Chem. Soc. Rev.* **26**, 21 (1997).
28. M. Lorenz and V. E. Bondybey, *Low Temp. Physics* **26**, accepted (2000).
29. V. E. Bondybey, J. H. English, and T. A. Miller, *J. Chem. Phys.* **70**, 1621 (1979).
30. V. E. Bondybey and J. H. English, *J. Chem. Phys.* **73**, 3098 (1980).
31. T. M. Halasinski, J. T. Godbout, J. Allison, and G. E. Leroi, *J. Phys. Chem.* **100**, 14865 (1996).
32. V. E. Bondybey and T. A. Miller, *J. Chem. Phys.* **70**, 138 (1979).
33. V. E. Bondybey and T. A. Miller, *J. Chem. Phys.* **73**, 3035 (1980).
34. T. J. Sears, T. A. Miller, and V. E. Bondybey, *J. Chem. Phys.* **74**, 3240 (1981).
35. P. Freivogel, J. Fulara, D. Lessen, D. Forney, and J. P. Maier, *Chem. Phys.* **189**, 335 (1994).
36. A. M. Smith, J. Agreiter, M. Härtle, C. Engel, and V. E. Bondybey, *Chem. Phys.* **189**, 315 (1994).
37. K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of diatomic molecules* (Van Nostrand Reinhold Company, New York, 1979).