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Laser Fluorescence Spectra of the Hexafluorobenzene Cation in Solid Argon

Sir:

While an impressive array of unstable molecules and free radicals have been studied by the matrix isolation technique, the list of ions studied this way is rather restricted. Since the identification of C_2^- by Milligan and Jacox,¹ numerous small ions have been observed²⁻⁹, mainly using infrared absorption spectroscopy. Particularly desirable would be studies of the electronic emission and excitation spectra of molecular ions. Since the totally symmetric modes are generally active in allowed electronic transitions, they should conveniently complement infrared observations and provide information about the ion's vibrational structures both in the ground and excited electronic states.

The fluorobenzene cations are an interesting group of polyatomic organic ions, which were recently observed in the gas phase emission using electron impact ionisation^{10,11}. The first ionizing transitions in these species are conveniently located¹² near 9.5 eV, and are probably further red shifted in the solid.¹³ They should thus easily be generated by the Lyman α radiation containing 10.2 eV of energy. In the present manuscript we report the observation of the emission and excitation spectra of $C_6F_6^+$ in solid argon. We deposited mixtures of the parent C_6F_6 with the Ar gas ($\approx 1:2000$) on a sapphire substrate cooled to 4.2 K and photolyzed simultaneously with the 1216-Å radiation. Excitation of the photolyzed deposits with the N_2 pumped dye laser results in an intense $C_6F_6^+$ fluorescence. Its gas phase lifetime¹¹ of 48 ns is only moderately shortened in the solid to ≈ 20 ns, and the fluorescence probably again occurs with near-unity quantum efficiency. A typical excitation spectrum of the $C_6F_6^+$ fluorescence is shown in Figure 1. The appearance of the emission spectrum is independent of the vibrational level used for excitation and implies an efficient and complete vibrational relaxation in the upper electronic state.

Molecular ions are known to interact with the rare gas solids to a considerably larger degree than neutral species. Actually, solvation energies of a variety of cations in solid Ar were reported¹³ to be of the order of 2 eV. It is gratifying that in spite of this strong interaction one can obtain mainly sharp zero phonon lines and a well-resolved vibronic structure. The line shapes of optical transitions in the solid environment are determined by the differences in the guest-host interaction potentials between the initial and final states. Apparently the interaction with the solid, while rather large in both the ground

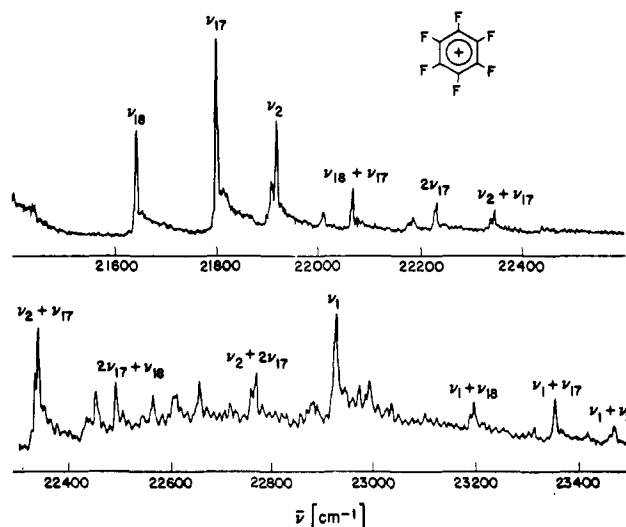


Figure 1. Excitation spectrum of the $C_6F_6^+$ fluorescence. The 0-0 emission at 21 372 cm^{-1} was monitored.

and excited electronic state, does not change appreciably during the electronic transition. In view of this strong interaction between ions and the solid host it is of particular interest to establish to what extent are the observed spectra representative of the free species. The recent observation of the gas phase $C_6F_6^+$ spectra¹⁴ makes such a comparison possible. The electronic origin undergoes a moderate 234- cm^{-1} red shift from its gas phase position, and all the observed vibrational frequencies are within experimental error of the gas phase values. It appears that matrix isolation studies can provide useful spectroscopic information even for ionic species.

Vibrational analysis of the $C_6F_6^+$ data leads to conclusions similar to those derived from our recent $C_6F_3H_3^+$ gas phase work.¹⁵ Some 30 vibronic bands are observed in our excitation spectrum and most of them can be interpreted in terms of vibrational frequencies of 270, 428, 547, and 1561 cm^{-1} and their overtones and combinations. The 1561- cm^{-1} frequency is clearly the totally symmetric C-F stretch, ν_1 . As could be expected, it is shifted in the positively charged species upward from the 1498- cm^{-1} value in the neutral molecule.¹⁶ The 547- cm^{-1} frequency can likely be attributed to the ring "breathing" mode, ν_2 , which occurs at 558 cm^{-1} in the parent.¹⁶

If the molecule has the full D_{6h} symmetry in both states one might expect only the two totally symmetric vibrations to occur strongly. It is clear from the spectrum in Figure 1 that several other vibrational modes appear with comparable intensities. The $C_6F_6^+$ cation thus seems to be distorted and have symmetry lower than D_{6h} in at least one of the two electronic states, probably due to Jahn-Teller distortion of the degenerate $^2E_{1g}$ ground state¹⁷. The low-frequency 270- cm^{-1} vibration and the 428- cm^{-1} frequency are therefore tentatively assigned to the E_{2g} in plane deformation vibrations ν_{17} and ν_{18} , which occur at 445 and 272 cm^{-1} , respectively,¹⁶ in the parent C_6F_6 . The observed vibronic bands and their tentative assignments are summarized in Table I.

Less vibrational information is obtained from the study of the emission spectra. Besides the 0-0 band, only three other relatively weak and sharp bands superimposed upon a broad continuum are seen and give values of 300, 444, and 557 cm^{-1} for the ground-state vibrational frequencies. These are tentatively assigned to ν_{18} , ν_{17} , and ν_2 , respectively. The broader appearance of the emission spectra may be due to the degeneracy of the ground electronic state and the resulting high density of states.

The work presented here clearly indicates that a considerable amount of useful information can be derived from the

Table I. $C_6F_6^+$ Excitation Spectrum in Solid Argon

cm^{-1}			cm^{-1}		
$\bar{\nu}$	$\Delta\nu$	assignment	$\bar{\nu}$	$\Delta\nu$	assignment
21 372	0	ν_{0-0}	22 606	1234	$\nu_{17} + 3\nu_{18}$
21 642	270	ν_{18}	22 659	1287	$3\nu_{17}$
21 800	428	ν_{17}	22 764	1392	$2\nu_{17} + 2\nu_{18}$
21 908	536	$2\nu_{18}$	22 775	1403	$\nu_2 + 2\nu_{17}$
21 919	547	ν_2	22 883	1511	
22 012	640		22 933	1561	ν_1
22 068	696	$\nu_{17} + \nu_{18}$	22 975	1603	$\nu_{15}?$
22 185	813	$\nu_2 + \nu_{18}$	22 996	1624	$\nu_{16} + \nu_{17}?$
22 231	859	$2\nu_{17}$	23 200	1828	$\nu_1 + \nu_{18}$
22 337	865	$\nu_{17} + 2\nu_{18}$	23 356	1984	$\nu_1 + \nu_{17}$
22 346	974	$\nu_2 + \nu_{17}$	23 476	2104	$\nu_1 + \nu_2$
22 456	1084	$2\nu_2$	23 625	2253	$\nu_1 + \nu_{17} + \nu_{18}$
22 495	1123	$2\nu_{17} + \nu_{18}$	23 785	2413	$\nu_1 + 2\nu_{17}$
22 568	1196	$\nu_{16}?$	23 896	2524	$\nu_1 + \nu_2 + \nu_{17}$

studies of electronic spectra of relatively large matrix isolated ions, providing insight both into the guest spectroscopy and into the ion-host interactions. Similar studies involving other ions as well as the effects of various hosts are in progress.

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A Trinuclear Molybdenum(IV) Cluster Compound Having an Unusual Structure and Unusual Stability

Sir:

The chemistry of molybdenum(IV) was relatively late and slow to develop and still remains imperfectly understood.¹ This is particularly true of its aqueous chemistry; only in 1966 was it shown² that Mo^{IV} is stable in aqueous media and only in 1973 did some firm information as to the identity of the species become available.³ There is also a very limited amount of information about its solid-state chemistry. We report here a discovery that bears significantly on both the aqueous and solid state chemistry of molybdenum(IV).

A solution of Mo^{IV} prepared by the method of Ardon and Pernick^{3a} was adsorbed on a Dowex 50W \times 2 cation-exchange column and was eluted with 0.5 M oxalic acid. CsCl was added to the eluate, and, upon slow evaporation of this red-purple solution, red-purple crystals were obtained. These crystals are monoclinic and belong to space group $P2_1/n$ with cell dimensions $a = 12.082$ (2), $b = 16.764$ (3), $c = 12.529$ (2) Å; $\beta = 91.31$ (2)°; $V = 2537$ (2); and $Z = 4$. Using 2500 unique reflections with $I > 3\sigma(I)$, the structure was solved and refined

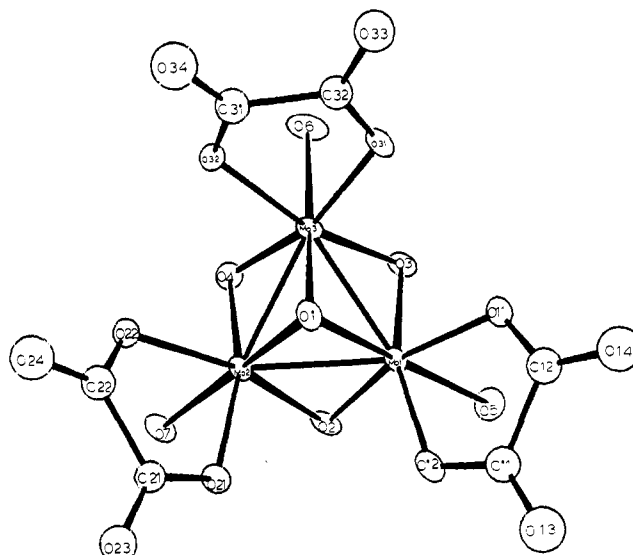


Figure 1. The structure of $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2+}$.

to convergence. Anisotropic temperature factors were used for the Mo and Cs atoms and for the oxygen atoms in the coordination sphere. The final residuals obtained are $R_1 = 0.041$, $R_2 = 0.061$. From the structure the complete formula is found to be $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3] \cdot 4H_2O \cdot 1/2H_2C_2O_4$.

The molecular structure and atom labeling scheme is shown in Figure 1. Each molybdenum atom is surrounded by six oxygen atoms in a distorted octahedral geometry. The average bond distance of Mo-O(1) (2.019 (6) Å) is slightly longer than that of Mo-O(a) (1.921 (7) Å) ($a = 2, 3, 4$; these atoms are chemically equivalent) as is expected for a triply bridging oxygen atom. The average Mo-O(H_2O) distance (2.154 (7) Å) and the average Mo-O(ox) distance (2.091 (7) Å) are as expected for these ligands. Other results are available as supplementary material.⁴

The most interesting distance in the structure is that between the molybdenum atoms, 2.486 (1) Å. This is clearly indicative of the presence of Mo—Mo bonds and, on the simple basis that Mo^{IV} has two d electrons with which a single bond could be formed to each of its neighbors, we believe that these Mo—Mo bonds are single bonds. They are considerably shorter than nearly all other previously recognized Mo—Mo single bonds⁵ and comparable in length with several recently discovered examples of what *may be* Mo=Mo double bonds, viz., $Mo_2(OPr^i)_6(CO)_6$ (2.489 Å) and $Mo_2(OPr^i)_8$ (2.523 Å). It must be kept in mind, however, that the lengths of all bridged M—M bonds, but especially when the bonds are of lower order, depend not only the bond order but also *strongly* on the number, size, arrangement, and character of the bridging groups.

The most pertinent structural comparison involving this structure is with the Mo_3O_{13} unit found in a series of compounds with the general formula $MM'Mo_3O_8$ where M and M' are two cations with charge totaling +4, e.g., Zn_2 , Co_2 , or $LiSc$.⁶ The Mo_3O_{13} unit, shown in Figure 2, is not discrete in these compounds, many of the oxygen atoms being shared between such units. In fact, this type of trinuclear cluster structure, which also occurs in the lower halides⁹ of niobium, Nb_3X_8 and $CsNb_4X_{11}$, has never before been found as a discrete entity. The present structure is, however, essentially the same, except that some of the 13 oxygen atoms are now supplied by oxalate ions and water molecules. It is the bridging oxygen atoms of the Mo_3O_{13} structure which are still simple oxygen atoms in the present case.

It is noteworthy that the electronic structure of the Mo_3O_{13} unit was analyzed many years ago¹⁰ and it was shown that a