The Laser Spectroscopy of Cool, Cold, and Very Cold Molecular Ions [and Discussion]

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The laser spectroscopy of cool, cold, and very cold molecular ions

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Molecular ions have long presented a challenge to spectroscopists. Because of the extreme difficulty in generating molecular ions in high concentrations, sensitivity limitations have restricted work in this field. The technique of laser-induced fluorescence (l.i.f.) has provided us with a means to partially overcome this limitation. L.i.f. spectra of small molecular ions, e.g. N_2^+, CO^+ and CO_2^+, show Doppler-limited resolution. Besides their spectroscopic information content, such spectra also serve as quantum-state selective ion detectors, by which dynamical processes involving such ions can be followed. L.i.f. spectra have also been recorded for larger organic ions, e.g. olefinic, acetylenic and benzenoid cations. The large molecular ions' spectral congestion, caused by the large number of levels populated at room or elevated temperatures, can severely limit the resolution and interpretability of the spectra. As a means of surmounting this problem, we have studied many of the cations at reduced temperatures. The techniques employed include liquid N_2 and free jet expansion cooling in the gas phase, and isolation in solid Ne matrices. The combination of these different spectra lead to a wealth of information about electronic structure, vibrational frequencies, Jahn–Teller effects, etc., in organic molecular ions.

1. Introduction

Molecular ions may be the most elusive of chemical intermediates. However, one can argue that they also may be among the most important of chemical intermediates. In the gas phase they are vital ingredients in electrical discharges and plasmas of all kinds. They are important in our own atmosphere and those of other planets. Likewise they are postulated to play key roles in the chemistry of interstellar clouds. They are also known to be present in shock waves and flames.

The spectroscopic methods presented in this paper are mainly aimed towards characterizing isolated molecular ions. None the less it is important to remember that ions are also of great importance in condensed phase chemistry. Many organic and inorganic reactions in solutions proceed by ionic intermediates; ionic environments are also encountered in many solids. For example, one can dope semiconductors with ionic species to yield materials for electronic devices. Even in such condensed-phase environments, the electronic and nuclear structure of the isolated ion is important to an understanding of its bonding and reactivity.

Traditionally the spectroscopy of ions has meant mainly mass spectroscopy. The principal reason for this fact is that, by and large, only ion counting has been a sensitive enough technique to detect gaseous ions. Simply because ion molecule reactions are in general the fastest chemical processes, ion densities are almost always quite low. (If one is fortunate enough to create ions in a vacuum, their density will still be limited by charge repulsion.) Although many techniques have been employed it has always proved extremely difficult in the laboratory to achieve molecular densities much above *ca.* 10^8 ions cm^{-3}, except in plasmas, where *ca.* 10^{10} ions cm^{-3} are possible. However, other problems are inherent with plasmas.

Mass spectroscopy, of course, gives us no information about an ion's structure or the

excitation of its internal degrees of freedom, rotational, vibrational and electronic. Until recently practically all our information on ion structure and quantum state distribution was very sparse and mainly supplied by optical emission spectroscopy. Slightly over 10 years ago Herzberg (1971) conveniently summarized the (non-mass) spectroscopy of molecular ions in a Faraday lecture to the Chemical Society. Only 39 molecular ions had been detected, 38 of which were either diatomic or triatomic; 32 of these ions had only been observed by optical emission spectroscopy, typically from discharge sources.
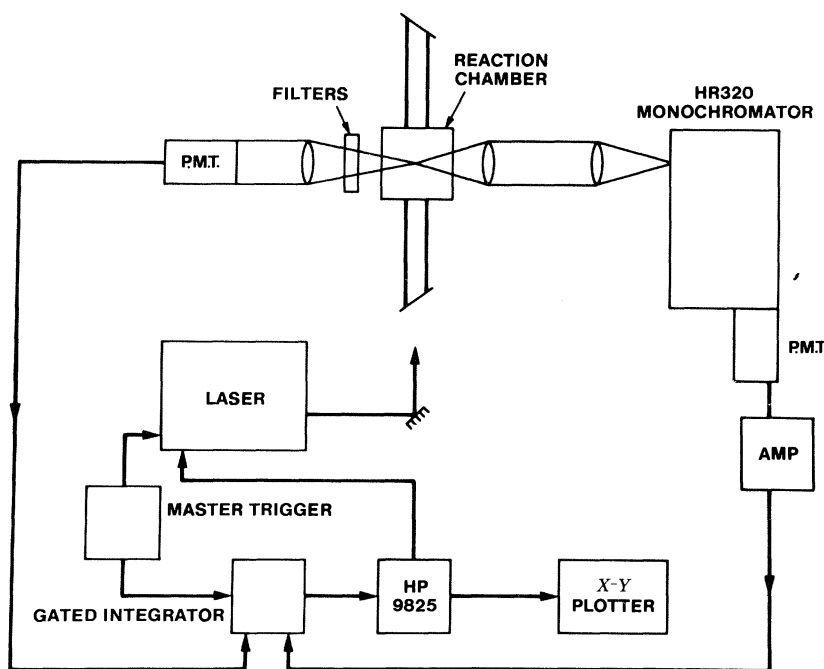

FIGURE 1. Schematic representation of apparatus for doing l.i.f. experiments on molecular ions. P.M.T., photomultiplier; HP9825, computer; AMP., amplifier.

Optical emission spectroscopy is useful for studying species in low concentrations like ions, because, assuming some production process, the excited state's radiative decay constant need only be faster than its reaction rate constant for observation. Because, next to counting ions, counting photons is the most sensitive spectroscopic technique, modest means of ion production enable one to obtain an optical emission spectrum.

Optical emission spectroscopy has continued to make important contributions to the study of molecular ions. However, its role is circumscribed in at least two important ways. On the one hand, optical spectroscopy is limited by the Doppler effect and so cannot supply the high resolution needed to obtain hyperfine structure, Zeeman effects, ultra-precise rotational constants, etc. Such properties are often needed to understand the details of an ion's electronic structure or to identify it in the interstellar medium. Much progress has been made in this area recently. Although there is no room in this paper to adequately describe this work, it has been the subject of an excellent recent review (Saykally & Woods 1981).

Besides being circumscribed from the point of view of resolution, simple optical emission spectroscopy is also limited in the amount of low-resolution information it can provide about molecular ions of considerable complexity. To understand this limitation, one need only

recognize that optical emission from molecular ions can only occur from an environment, such as a discharge or plasma, that is energetic enough to ionize molecules and electronically excite the ions. Generally such an environment would also be expected to produce species with considerable excitation of their internal degrees of freedom. Such vibrationally and rotationally 'hot' ions will give rise to relatively congested spectra. For organic molecules fragmentation may well also occur. In any case, spectra of moderately sized molecules in this environment may easily become so congested as to lose all information content.

What generally is needed, then, for moderately sized organic ions is a spectroscopic technique that separates ion production and detection while retaining the sensitivity of photon counting. Such a technique is laser-induced fluorescence (l.i.f.) of molecular ions. L.i.f. shares with mass spectroscopy and optical emission spectroscopy the advantages of great sensitivity. Moreover, like optical emission spectroscopy it gives quantum state information about molecular ions. Indeed, in some ways, it is superior in this respect, for it probes directly the ground state of the ion. Perhaps most importantly, it has great flexibility in the sampling of ions. Thus molecular ions can be created and then subjected to a gentler or cooler environment for interrogation.

In the remainder of the paper we first briefly look at some of the details of the l.i.f. technique. Then we survey the results that we have obtained with molecular ions in three quite different environments designed to produce cool, cold, and very cold molecular ions.

2. PRINCIPLES OF LASER-INDUCED FLUORESCENCE

Figure 1 shows the general principles underlying an l.i.f. experiment on molecular ions. Probably the most crucial feature of such an experiment is the sample or reaction chamber wherein molecular ions are prepared or reside or both. This part of the apparatus differs in different experiments and we shall discuss it in detail in subsequent sections, but for the moment we shall concentrate on the aspects of the apparatus common to all experiments.

To perform l.i.f. of molecular ions, one requires a tunable dye laser operating in the spectral region of the ion's absorption. In our experiments we have used either a N_2 (Molectron UV-24) pumped dye laser (Molectron DL-II) or a flashlamp-pumped dye laser (Chromatix CMX-4). As shown in figure 1 the laser beam interrogates the molecular ion sample. If the laser frequency is tuned to resonance with a molecular ion's absorption, assuming the excited ionic state has a reasonable quantum yield for emission, laser-induced fluorescence is produced. The fluorescence perpendicular to the laser beam is collected in a temporally gated fashion.

On the left-hand side of figure 1 is shown a simple photomultiplier detector (with minimal wavelength filtering) for the detection of total fluorescence. If the output of the photomultiplier is plotted against the tuned laser frequency one obtains a (total fluorescence) excitation spectrum of the molecular ion of interest. Once the excitation spectrum is available, the laser frequency can be tuned to coincide with a feature in that spectrum. Then the laser-induced fluorescence generated can be dispersed by a monochromator as shown on the right-hand side of figure 1. A plot of the output of the photomultiplier on the monochromator against monochromator wavelength yields a (laser-excited) wavelength-resolved emission spectrum.

The excitation spectrum, except for 'hot bands', primarily gives information about the excited electronic state of the ion. Likewise the wavelength-resolved emission spectrum primarily gives information about the ground (or lower) electronic state. Moreover, since different upper electronic state levels can be selectively excited, the ground-state information can be

further compartmentalized. This subdivision of a complex spectrum can aid greatly in its analysis.

In table 1 we list the general categories of molecular ions that have been studied by l.i.f. techniques. As table 1 shows, the ions range from simple diatomics to complex organic cations. For many of the diatomic and triatomic species, the spectroscopy is well in hand from traditional optical emission studies. Thus laser-induced fluorescence serves mainly as a quantum-state selective detector of these ions. As the emphasis of this paper is on spectroscopy rather than dynamics, we shall concentrate our attention upon the larger cations, whose spectroscopy has hitherto been largely unexplored.

TABLE 1. CATEGORIES OF MOLECULAR IONS FOR WHICH L.I.F. SPECTRA HAVE BEEN OBSERVED

(Illustrative examples are given for each category.)

diatomic ions	N_2^+, CH^+, CO^+
triatomic ions	CO_2^+, CS_2^+, $BrCN^+$
acetylenic ions	$H-(C\equiv C)_2-H^+$, $Cl-(C\equiv C)_2-H^+$, $N\equiv C-C\equiv C-C\equiv N^+$
olefinic ions	$H_2C=C-C=C-C=CH_2^+$
	H H H H
benzenoid ions	$C_6F_6^+$, $C_6H_3Cl_3^+$, $C_6F_5OH^+$

3. PENNING IONIZATION

The first report of l.i.f. of a molecular ion was for N_2^+ by Engelking & Smith (1975). The next reports of l.i.f. in ions were in 1977 for CO^+ (Miller & Bondybey 1977) and CO_2^+ (Bondybey & Miller 1977). Very quickly thereafter a significant breakthrough followed when the same workers reported the l.i.f. spectra of several large organic cations, first the 1,3,5-trifluorobenzene cation (Miller & Bondybey 1978) and then several other fluorobenzene cations (Bondybey & Miller 1979). In the few years since those initial reports the field has rapidly expanded. L.i.f. techniques have now been used to study over 40 molecular ions, with over three dozen of these species being polyatomic (Miller 1982).

All the initial l.i.f. experiments, and probably still most of the l.i.f. experiments, have used the Penning ionization process to produce the molecular ions. A schematic representation of this apparatus is shown in figure 2. Metastable inert gas atoms (He*, Ar*, etc.) are produced in a d.c. discharge upstream of the reaction chamber. Mixing between a reagent gas and the metastable atoms occurs in a conical region in the reaction chamber downstream from the discharge tube inlet. The tip of the mixing zone is centred in the viewing windows and is crossed with the laser beam. In the Penning process the metastable atom's energy is used upon collision to eject an electron from the reagent and form a positively charged molecular ion.

There are at least a couple of reasons why the Penning ionization process is quite appropriate for l.i.f. studies. The energies of the metastable inert gas atoms, from 8.3 eV for $1s_5$ Xe to 19.8 eV for 2^3S He, span a sufficient range so that it is energetically possible to ionize practically any molecule, yet by proper choice of metastable not give the ion a huge excess of energy. (While ionization is almost always possible, competing pathways leading to dissociation, etc., are not precluded.) In favourable cases, the energy of the metastable is sufficient to ionize the molecule, but insufficient to produce any electronically excited states of the ion. In this case the ion is produced in a completely 'dark' environment, favourable to the l.i.f. experiment. In other cases, where more energy is present, the production of ions may be accompanied by
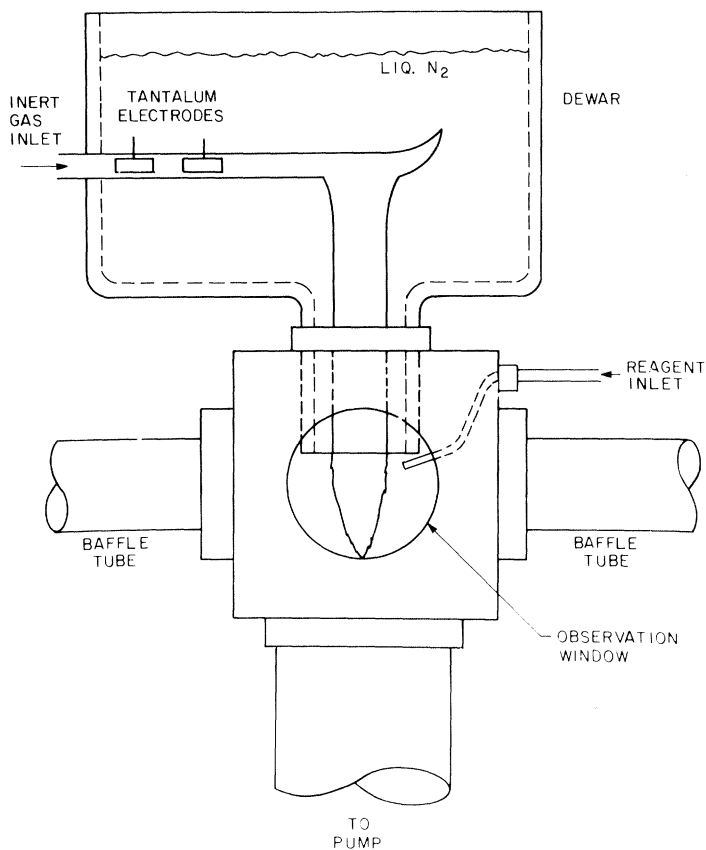
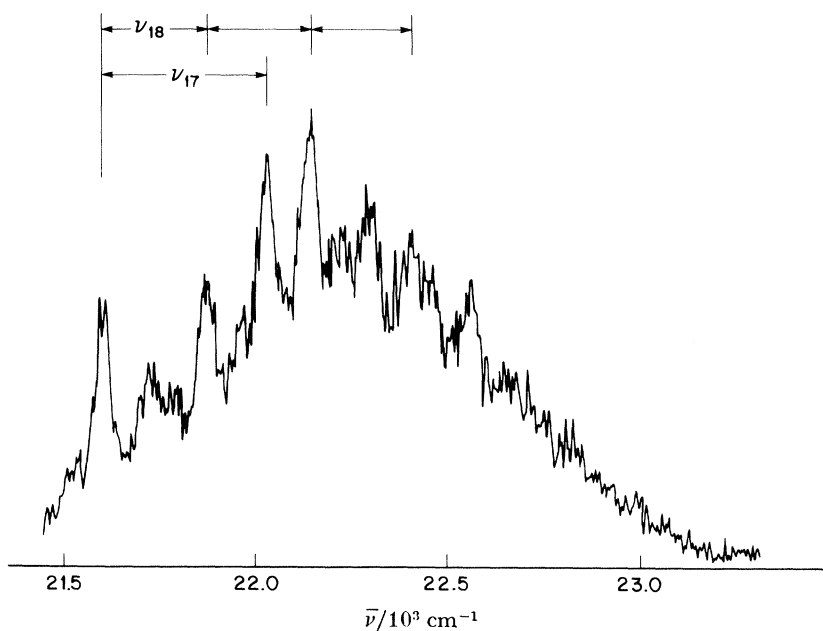FIGURE 2. Schematic representation of apparatus for producing molecular ions for l.i.f. by Penning ionization.

FIGURE 3. L.i.f. excitation spectrum of gaseous $C_6F_6^+$ at room temperature.

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electronic excitation and chemiluminescence. This, of course, does not preclude the observation of l.i.f., but merely makes it more difficult.

For the purpose of the present discussion probably the most important advantage of the Penning production of ions for l.i.f. is their temperature control. In an l.i.f. experiment on a population of ions produced by Penning ionization, there are on average many collisions between the ions and the large excess of ground-state inert gas atoms, before the ions are interrogated by the laser. Such collisions allow the rotational and vibrational temperature of the ions to equilibrate with the translational temperature of the bulk gas. Thus, even if the ions are produced 'hot', one can obtain a 'cooled' l.i.f. spectrum of them.
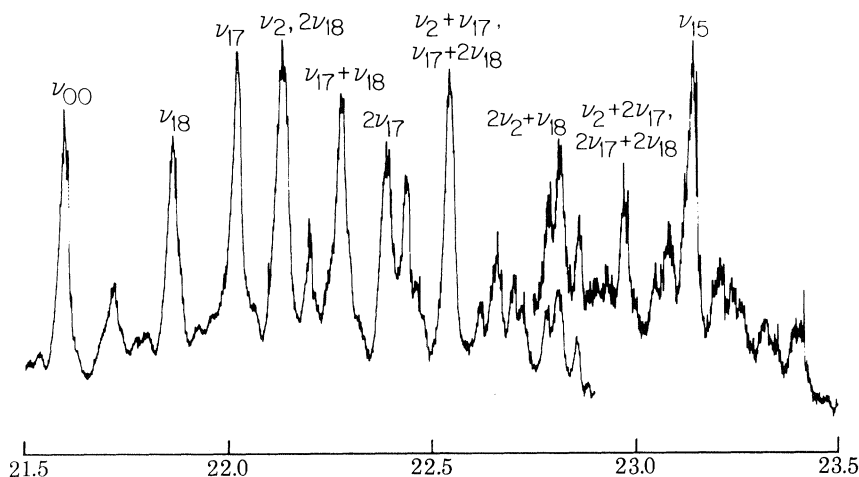

FIGURE 4. L.i.f. excitation spectrum of gaseous $C_6F_6^+$ taken at near liquid N_2 temperature.

For the remainder of this paper we shall use the hexafluorobenzene cation, $C_6F_6^+$, to illustrate the effect of environment upon the l.i.f. spectra of complex ions. The l.i.f. spectra are all taken for the electronic transition $\tilde{B}\ ^2A_{2u} \leftrightarrow \tilde{X}\ ^2E_{1g}$. Figure 3 shows (Bondybey & Miller 1978) the l.i.f. excitation of $C_6F_6^+$ taken with the He carrier gas at near-ambient temperature, and there is every reason to believe that the $C_6F_6^+$ in this spectrum is rotationally and vibrationally roughly equilibrated to ambient temperature. Indeed if one compares the spectrum in figure 3 with an optical emission spectrum taken from a discharge source (Cossart-Magos et al. 1979), one can see considerably less spectral congestion in figure 3. None the less, figure 3 is clearly limited in information content by its congestion and overlap.

Figure 4 shows (Sears et al. 1981a) a very similar l.i.f. excitation spectrum of $C_6F_6^+$, except in this case the He carrier gas was cooled to near liquid N_2 temperature. The improvement in resolution is truly remarkable. One can clearly make vibrational assignments with some confidence here. Indeed it is clear that this spectrum can be assigned in terms of progressions in both a_{1g} and e_{2g} vibrational modes. The clear-cut existence of the e_{2g} progression shows at a minimum that $C_6F_6^+$ does not possess full D_{6h} symmetry in both electronic states involved in this transition. Since the ground state of $C_6F_6^+$ is the doubly degenerate $^2E_{1g}$ state, it is extremely likely that the appearance of the e_{2g} progressions in the spectrum is caused by a Jahn–Teller distortion of the ground state (Jahn & Teller 1937; Longuet-Higgins 1961).

It would, however, be unfair to claim that the l.i.f. spectrum of $C_6F_6^+$ in figure 4 resolves all

ambiguities. For instance, it is not clear whether the unmarked band between those marked ν_{00} and ν_{18} is a unique vibrational frequency in the excited electronic state or a 'hot' band. Similarly, the band marked ν_2, $2\nu_{18}$ is assigned to a completely unresolved blend of these two transitions. To overcome these difficulties, l.i.f. spectra of still colder $C_6F_6^+$ are required.

4. MATRIX-ISOLATED MOLECULAR IONS

In order to make the spectra of complex organic ions simpler, we have tried to make them even colder by isolating them in an inert gas matrix cooled to liquid He temperature. Figure 5 shows a schematic diagram of a matrix isolation apparatus. In a typical experiment, a mixture
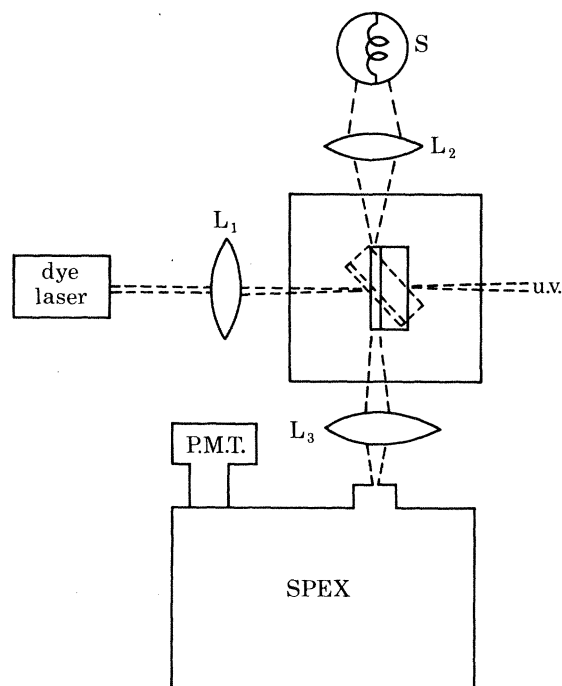

FIGURE 5. Schematic diagram of apparatus for l.i.f. studies on matrix isolated ions. L, lens; SPEX, monochromator; S, light source for absorption studies.

of about 100–1000 μg g^{-1} of the parent neutral in an inert gas is deposited over a period of 1–3 h on a sapphire window held at ca. 5 K by liquid He. Ne is certainly the preferred inert gas to minimize matrix perturbations, but in some cases Ar is also acceptable. As shown in figure 5, by rotating the sample, it can be exposed to vacuum u.v. radiation, e.g. Ly α at 121.6 nm. Initially the concentration of ionic species increases approximately linearly with vacuum u.v. exposure time, but typically after a minute or so a photostationary state is reached with no further apparent increase in ion concentration.

After the ions are produced, they can be studied at leisure by l.i.f. techniques. As in the gas phase, two kinds of l.i.f. spectra can be recorded, excitation spectra and wavelength-resolved emission spectra. While in the gas phase 'total' excitation spectra (where all the laser-excited fluorescence is collected) are the rule; in the matrix, they are the exception. Usually an excitation spectrum is obtained by tuning the monochromator to an emission feature and scanning the laser. The monochromator selects from the several possible matrix sites only those that emit

in a narrow bandpass, resulting in a reduced inhomogeneous line width and a sharp, site-selected excitation spectrum.

Obviously one experiences a considerable loss in light-collection efficiency with the mono-chromator, but the much higher ion concentration (not less than 10^{14} ions cm^{-3}) obtainable in the matrix allows the maintenance of an excellent signal:noise ratio. Moreover, in the matrix, vibrational relaxation is generally very rapid compared with radiative emission from an excited electronic state. No matter what vibrational transition is excited in the upper electronic state, monitoring of the strongest transition emanating from the excited state's vibrationless level will insure the collection of the bulk of the l.i.f.
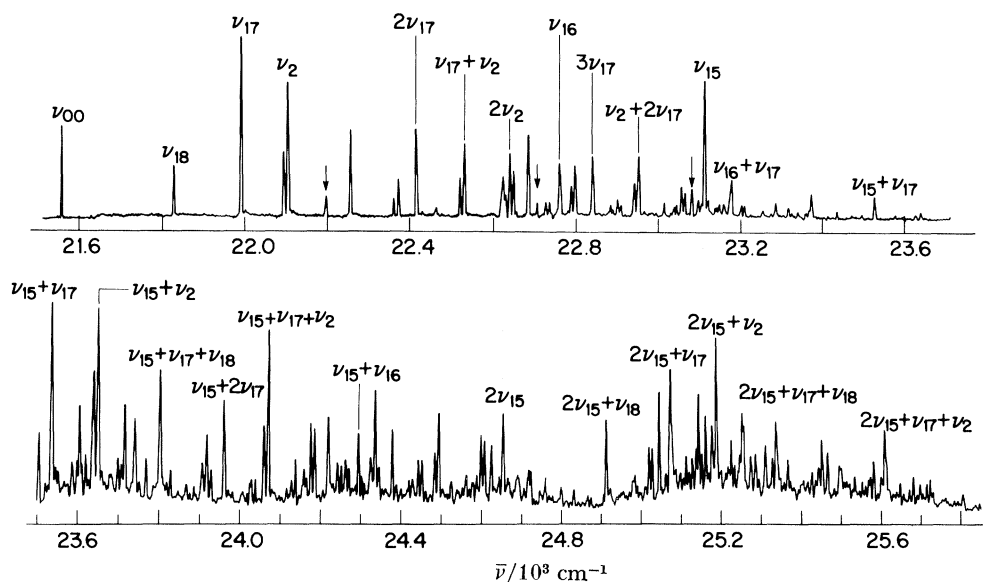

FIGURE 6. L.i.f. excitation spectrum of $C_6F_6^+$ in a Ne matrix.

Figure 6 shows (Bondybey & Miller 1980) the l.i.f. excitation spectrum of $C_6F_6^+$ isolated in a Ne matrix. Obviously the resolution of this spectrum is superior to those in figures 3 and 4. Certain of the ambiguities in figure 4 can be immediately resolved. The band in figure 4 marked ν_2, $2\nu_{18}$ is clearly resolved in figure 6. In a similar way, we see that the band between ν_{00} and ν_{18} in figure 4 has disappeared in figure 6, establishing that it is a 'hot' band. The signal:noise ratio and resolution obtainable for the l.i.f. spectrum of $C_6F_6^+$ in a Ne matrix is sufficiently high that one can easily obtain useful vibronic information more than half an electronvolt above the origin, as the lower trace of figure 6 shows.

The key question is, however, to what extent the Ne matrix spectrum can be considered the low temperature limit of the gas phase spectrum. In other words, has the Ne matrix perturbed the l.i.f. spectrum? A casual examination of the spectra in figures 4 and 6 shows very con-siderable similarity. In table 2 the comparison is made more quantitative by a listing of all the band frequencies observed within 1500 cm^{-1} of the origin both in the matrix (Bondybey & Miller 1980) and in the gas phase (Sears *et al.* 1981*a*; Miller *et al.* 1980). Table 2 shows that the two spectra are not exactly identical, but most of the differences are simply explicable.

We note that there is an overall shift of 59 cm^{-1} to lower frequency of the $C_6F_6^+$ spectrum in the Ne matrix compared with the gas phase. There are also some lines that appear only in the matrix or only in the gas phase. However, all the identified lines present only in the gas phase

TABLE 2. BANDS OF $C_6F_6^+$, OBSERVED WITHIN 1500 cm^{-1} OF THE ORIGIN IN THE GAS PHASE AT LIQUID N_2 TEMPERATURE, AND IN A Ne MATRIX

gas-phase frequency/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}	Ne-matrix frequency/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}	assignment
21 617	0	21 558	0	origin
21 716	99	—	—	17^1_1 ($\frac{1}{2}$)
21 739	122	—	—	18^1_1 ($\frac{1}{2}$)
21 796	179	—	—	$17^0_1 18^2_1$ ($\frac{5}{2}$)
21 821	204	—	—	$17^1_2 18^1_0$ ($\frac{1}{2}$)
21 885	268	21 823	265	18^1_0
21 945	328	—	—	$17^1_1 18^1_1$ ($\frac{5}{2}$)(?)
21 987	370	—	—	18^2_1 ($\frac{3}{2}$)
22 042	425	21 984	426	17^1_0
22 084	467	—	—	(?)
22 156	539	22 088	530	18^2_0
		22 098	540	2^1_0
22 226	609	22 189	631	a^2_0 (?)
22 309	692	22 247	689	$17^1_0 18^1_0$
22 420	803	22 352	794	18^3_0
		22 364	806	$2^1_0 18^1_0$
22 427	850	22 406	848	17^2_0
22 439	875	—	—	(?)
22 507	890	22 453	895	$a^2_0 18^1_0$
22 573	956	22 511	951	$17^1_0 18^2_0$
—	—	22 521	963	$2^1_0 17^1_0$
22 649	1032	22 611	1053	$a^2_0 17^1_0$
—	—	22 618	1060	18^4_0
—	—	22 628	1070	$2^1_0 18^2_0$
22 693	1075	22 636	1078	2^2_0
22 732	1115	22 672	1114	$17^2_0 18^1_0$
22 750	1133	22 694	1136	b^2_0
—	—	22 716	1158	$a^2_0 18^2_0$
—	—	22 724	1166	$a^2_0 2^1_0$
22 813	1196	22 748	1190	16^1_0
22 841	1224	22 787	1229	$2^1_0 17^1_0 18^1_0$
22 887	1272	22 830	1272	17^3_0
22 931	1314	22 875	1317	$a^2_0 17^1_0 18^1_0$
—	—	22 881	1323	18^5_0
—	—	22 894	1336	$2^1_0 18^3_0$
22 957	1340	22 904	1344	$2^2_0 18^2_0$
23 002	1385	22 934	1376	$17^2_0 18^2_0$
—	—	22 945	1387	$2^1_0 17^2_0$
—	—	22 959	1401	$b^2_0 18^1_0$
23 075	1458	23 008	1450	$16^1_0 18^1_0$
—	—	23 033	1475	$a^2_0 17^2_0$
—	—	23 040	1482	$17^1_0 18^4_0$
23 111	1494	23 052	1494	$2^1_0 17^1_0 18^2_0$

are assigned as hot bands and should therefore be absent in the matrix. Similarly, especially at higher frequencies, there are a few lines identified only in the matrix. However, in all cases these are quite weak lines with insufficient signal:noise to be expected to be observed in the gas phase. There are also a few pairs of lines unresolved in the gas phase that do clearly resolve in the matrix. For the remaining lines, agreement in the $\Delta\bar{\nu}$ value is always within 10 cm^{-1}, with the great majority within 5 cm^{-1}, well within experimental error. (The only exception to this statement appears to involve the so-called mode a, which is probably an overtone in some non-allowed symmetry species – perhaps an out-of-plane vibration. In this one case occasional discrepancies twice the above limits are observed.)

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Because all the transitions involved in the excitation spectrum of $C_6F_6^+$ in solid Ne originate in the vibrationless level of a non-rotating molecule, the spectrum provides very little information about the ground-state structure of $C_6F_6^+$. However, this information can be provided in considerable detail by the other kind of l.i.f. spectrum discussed in §2, namely the laser-excited wavelength-resolved emission spectrum. Such a spectrum for $C_6F_6^+$ in solid Ne is shown (Bondybey & Miller 1980) in figure 7. As mentioned previously, vibrational relaxation in the
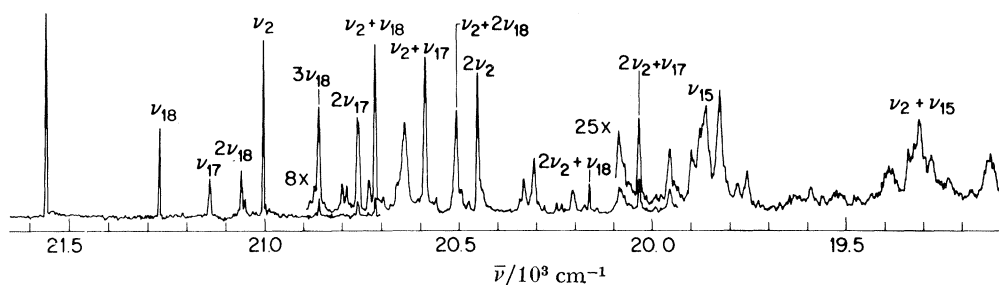

FIGURE 7. L.i.f. wavelength-resolved emission spectrum of $C_6F_6^+$ in solid Ne.
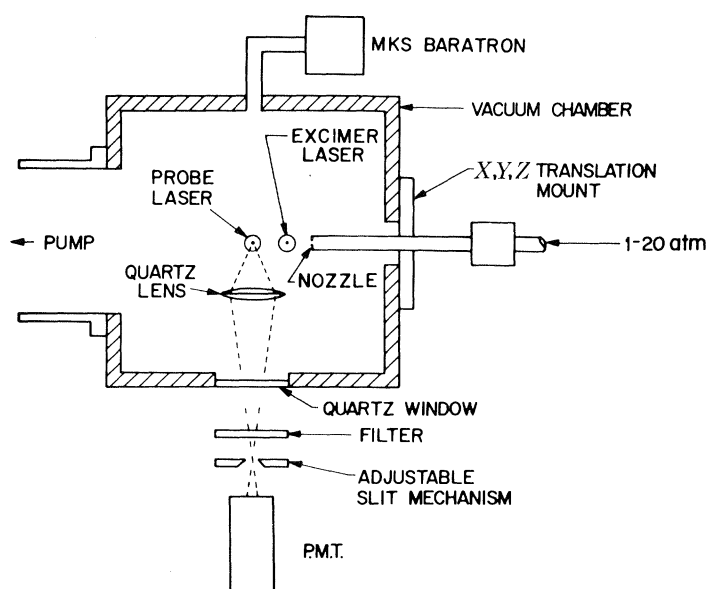

FIGURE 8. Schematic diagram of apparatus for producing ions by multi-photon ionization in a free jet expansion.

matrix is very rapid, so all the transitions in figure 7 arise from emissions out of the excited electronic state's vibrationless level. The spectrum is thereby simplified in that it represents emission from a single, rather than many, excited state levels. On the other hand, one can see that there is extensive vibrational information about the ground state contained in that spectrum.

One can note from figures 4 and 6 and table 2 that the vibrational structure in the excited $\tilde{B} \, ^2A_{2u}$ state of $C_6F_6^+$ is very regular and harmonic. On the other hand, the vibrational structure of the ground $\tilde{X} \, ^2E_{1g}$ state of $C_6F_6^+$, as revealed by figure 7, is very irregular and shows no

harmonic progressions, except for the a_{1g} mode ν_2. All the e_{2g} modes show very irregular structure. This is exactly what would be expected for a Jahn–Teller distortion of this ion's ground state, and from this information a good deal about that distortion can be learned (Sears *et al.* 1981*b*).

It is clear from table 2 that to a very good approximation the Ne matrix excitation spectra give unperturbed information about the structure of the $\tilde{B}$ $^2A_{2u}$ state of $C_6F_6^+$. One might reason by analogy that the information about the $\tilde{X}$ $^2E_{1g}$ state would be similarly unperturbed. However, because of the differences in the potentials in the two states, and particularly the existence of the Jahn–Teller effect in the latter, this assumption is not unchallengable. Thus, we (Sears *et al.* 1980) have independently carried out laser-excited wavelength-resolved emission studies with the Penning ionization apparatus. Because of signal:noise considerations neither the resolution is as good nor the number of bands examined is as great in the gas phase as it is in the matrix. None the less the information is more than sufficient to demonstrate that as with the $\tilde{B}$ state, the $\tilde{X}$ state vibronic structure is essentially unperturbed by the Ne matrix.

5. Free jet expansion cooling of ions

Although there is now a good body of evidence that vibrational structure of organic ions is nearly unperturbed by a Ne matrix, there remain ample reasons to desire a gas-phase technique for producing ions cooled to similar temperatures. Matrix shifts, and spectral congestion in warm spectra, mean that the only accurate way to determine the origins of electronic transitions is from very cold gas-phase spectra. Because rotational structure is quenched by a matrix, this kind of information can only be obtained in the gas phase. Finally, although most evidence points to minimal perturbation in a Ne matrix, only in the gas phase can one always be positive that one is dealing with isolated ion properties.

To prepare gas-phase ions with internal temperatures of a few degrees Kelvin or less, we have turned to the free jet expansion technique (Levy 1980). Figure 8 shows a schematic diagram of our apparatus. The heart of the experiment is a very small nozzle, typically *ca.* 150 μm in diameter. A species of interest, for the present example C_6F_6, is entrained in a carrier gas, e.g. He or Ar, at a high pressure, *ca.* 1–20 atm (*ca.* 0.1–2 MPa), behind the nozzle. As the gas expands through the nozzle into the vacuum chamber, it is cooled adiabatically. The translational temperature of an ideal gas is easily calculated (Levy 1980) from thermodynamic principles, and one finds that for backing pressures within the range mentioned above, temperatures of the order of 1 K can be obtained downstream of the nozzle. For most large molecules, the internal degrees of freedom will be equilibrated, or nearly so, with the translational temperature.

This technique provides very cold neutral molecules in the gas phase. It remains to convert them into ions without substantially perturbing their quantum-state distributions. There have been several reports (Carrington & Tuckett 1980; Tuckett 1981; Miller *et al.* 1980; De Koven *et al.* 1981; Maier *et al.* 1981) of using electrons to produce ionization and emission from cold ions. In none of these experiments has l.i.f. been obtained. For the purpose of this paper, let us emphasize another technique, multi-photon ionization (Heaven *et al.* 1982). Optical selection rules guarantee that little rotational warming of the molecule can occur upon ionization. Vibrationally, excitation is usually governed by the overlap of the vibrational wavefunctions, i.e. Franck–Condon considerations. For a molecule like C_6F_6, and also for many other molecules,

the Franck–Condon factors will be nearly diagonal so very little vibrational excitation occurs upon ionization.

In our experiments we have used an ArF laser for the photoionization step. The energy of two ArF photons is just under 13 eV, sufficient to ionize most organic compounds without being excessive. Figure 9 shows the spectrum of $C_6F_6^+$ produced in this manner. By comparing figures 4 and 9 it is clear that the jet-cooled $C_6F_6^+$ is much colder than that produced in the liquid N_2
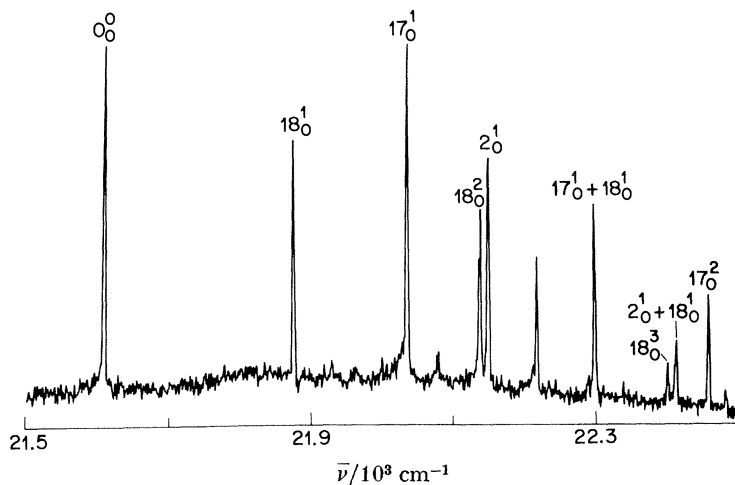

FIGURE 9. L.i.f. excitation spectrum of $C_6F_6^+$ produced by two-photon ionization of C_6F_6 in a free jet expansion.

cooled Penning ionization apparatus. Indeed the spectrum is so cold that it is difficult to determine its exact temperature. There is no sign of hot bands originating from any vibrationally excited level of the ground state. Likewise there is no evidence for rotational contours; the bandwidths are primarily limited by the laser line width, which is 1 cm^{-1} in this example. (Further experiments are planned with a narrower laser.)

Most gratifying about the free jet spectrum of $C_6F_6^+$ is the confirmation of some of our early findings for the Ne matrix spectrum. One can see that the ν_2 and $2\nu_{18}$ bands are now resolved, just as in the matrix spectrum. Similarly the band between ν_{00} and ν_{18} in figure 4, which was judged to be a hot band based upon the matrix spectrum, is, as expected, absent from figure 9 as well.

Besides the opportunity to study bare, gaseous ions at very low temperatures, the free jet expansion technique allows for the first time the study of ionic clusters by l.i.f. techniques. Figure 10 shows again a free jet l.i.f. excitation spectrum of $C_6F_6^+$ but under slightly different conditions. The stagnation pressure behind the jet is 4 atm (ca. 0.4 MPa) of a 10% Ar–He mixture. The laser is scanned over a slightly lower frequency region, with the sharp line at the right-hand side of the scan corresponding to the ν_{00} band of the bare $C_6F_6^+$. The sharp line structure at the left-hand side of the scan corresponds to l.i.f. of C_2 produced by ArF photolysis. The most interesting aspect of the spectrum in the relatively broad feature located ca. 230 cm^{-1} below the ν_{00} band of $C_6F_6^+$. Under these conditions it is found that all the bands of the $C_6F_6^+$ spectrum have broad satellites about 230 cm^{-1} to lower frequency (as one progresses above ν_{00}, the spectrum soon becomes cluttered, owing to the overlap of the many bands present).

This broad-lined spectrum may be attributed to ionic clusters of the form $C_6F_6^+ \cdot Ar_n$. Interestingly the observed shift of the cluster spectrum of 230 cm^{-1} is very nearly the same as the red shift of 245 cm^{-1} measured for $C_6F_6^+$ in a solid Ar matrix (Bondybey & Miller 1980; Miller *et al.* 1980). This is rather surprising because the number of Ar's clustered about $C_6F_6^+$ must be relatively small. However, there is at least indirect evidence from the matrix studies
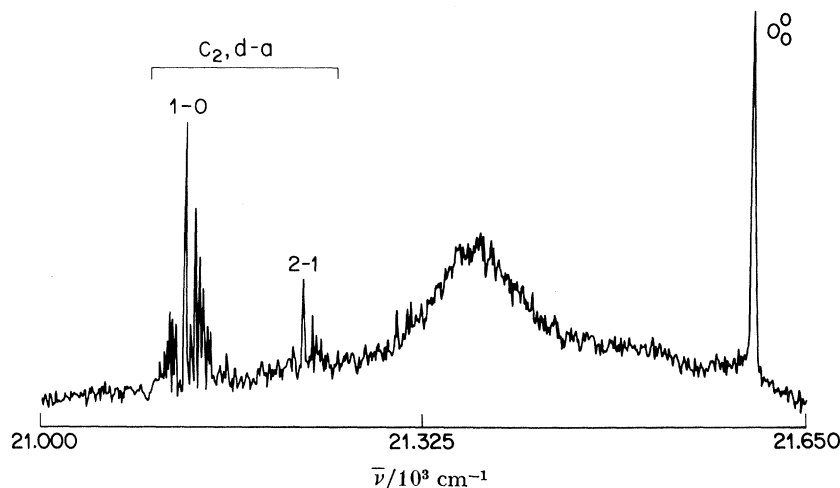

FIGURE 10. L.i.f. excitation spectrum showing a cluster, $C_6F_6^+ \cdot Ar_n$, whose origin transition is the broad line in the centre of the scan.

(Bondybey & Miller 1980) that the first two Ar's, which are probably bonded above and below the ring, likely provide most of the change in the electronic environment responsible for the spectral shift. Thus the similarities of the shifts may not be so surprising.

In other ways, however, the cluster l.i.f. spectrum is quite different from that obtained in the matrix. The l.i.f. excitation of $C_6F_6^+$ in an Ar matrix at 5 K shows quite sharp bands like those exhibited in the Ne matrix (figure 6). The cluster bands are 10–100 times broader. It is likely that some broadening is created by clusters, $C_6F_6^+ \cdot Ar_n$, with different numbers of Ar. However, the argument that most of the spectral shift is accounted for by the first two Ar's would seem to make it unlikely that the totality of the broadening can be explained in this way.

Rather, it appears that the most likely explanation is that the clusters are significantly warmer (at least tens of kelvins) than the Ar matrix and that the higher temperature leads to broadening by sequence congestion, etc. Some of this warmth may come from the heat of formation liberated when the $(n+1)$th Ar accretes to a cluster, $C_6F_6^+ \cdot Ar_n$. However, it is likely that the cluster must be fairly large before the probability of accretion is very great. Indeed, formally, simple accretion would always form a metastable species, just as the collision of two atoms can form only a transient diatomic species unless a third body is present to carry away excess energy.

The most likely process for the initial formation of an ionic cluster is the ionization of a neutral van der Waals cluster formed by three-body collision in the initial stages of the expansion (Levy 1980). Interestingly, such a mechanism would probably lead to an ionic cluster with a number of vibrational degrees of freedom excited, i.e. vibrationally 'hot'. This mechanism is illustrated in figure 11. The binding potential for an Ar atom in a neutral van der Waals cluster is very shallow, while it is relatively deep in an ionic cluster. By the Franck–Condon principle,

transitions into the vibrationally excited portion of the ionic potential curve are favoured. Because there are many degrees of freedom, including that of the leaving electron carrying excess energy, a number of different vibrational levels will have comparable probabilities for excitation. This will lead to a number of sequence and other 'hot' bands that will probably be reflected in a broaden spectral transition.
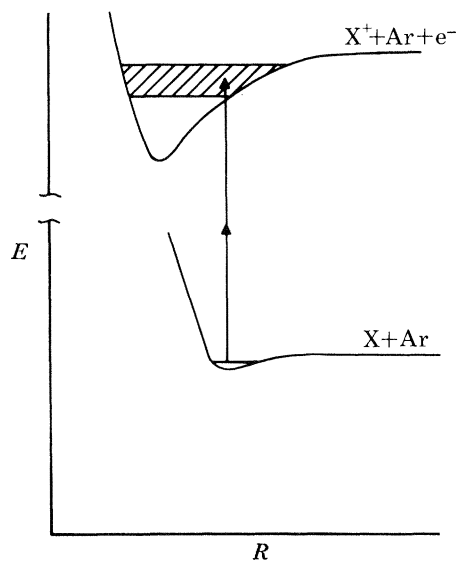

FIGURE 11. Schematic diagram illustrating the two-photon ionization of a neutral cluster to form an ionic one. The variable R designates an idealized coordinate giving the C_6F_6 distance to a departing Ar atom.

6. CONCLUSIONS

L.i.f. fluorescence spectroscopy has proved itself to be a versatile method for studying molecular ions. For large molecular ions, the control of 'temperature', i.e. the population distribution in internal quantum states, is critical for the understanding and analysis of the spectrum. Three entirely separate techniques, Penning ionization, matrix isolation and free jet expansion, have proved very useful for this purpose. The combination of data from the three different techniques has allowed a detailed understanding of the electronic and geometric structure of numerous organic cations, including such subtle effects as Jahn–Teller interactions (Sears *et al.* 1981 *b*). The combination of the spectra of ions in matrices with the recently discovered (Heaven *et al.* 1982) cluster ion spectra obtained from free jet expansions opens the door to numerous studies concerning the interactions and bonding of ions with neutral molecules.

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Discussion

R. P. TUCKETT (*Department of Physical Chemistry, University of Cambridge, U.K.*). In the last part of his paper, Dr Miller described experiments on the fluorenbenzene cations produced by two-photon excitation by using a pulsed u.v. excimer laser via a virtual intermediate state. This ionization technique seems to have the attraction of energy selectivity (only the ground states of these ions are produced), which electron impact ionization and (to a lesser extent) Penning ionization do not have. Could he comment on the relative efficiency of these different ionization processes?

T. A. MILLER. The two-photon ionization experiments are at an early stage and much work remains to be done. However, it is already clear that multi-photon production of ions for spectroscopic studies offers an attractive alternative to other techniques, such as electron impact and Penning ionization. We have made no direct measurements of the relative efficiencies of these processes. However, based upon our observed spectra, it appears that all three of these methods produce comparable (within one to two orders of magnitude) ion densities.