ADVANCES IN CHEMICAL PHYSICS—VOLUME LX

I. Prigogine and Stuart A. Rice—Editors

PHOTODISSOCIATION AND PHOTOIONIZATION

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AND
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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new reasearch and serve as a personalized learning text for beginners in a field.

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MULTIPHOTON IONIZATION OF GASEOUS MOLECULES*

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I. INTRODUCTION

Multiphoton ionization (MPI) has been around for quite a long time and is too varied and complex a subject to review succinctly. We will therefore limit our comments to areas of interest to chemists, and in particular to the ionization of molecules and gaseous free radicals. We will not discuss the ionization of atoms, which has been studied thoroughly by the atomic physics community, even though a great deal of very thoughtful research has transpired in this area. For the reader who is interested in this subject, or who would like to see the theory developed in the most complete and elegant forms, we refer to recent reviews concerning the MPI of atoms.[1,2] Also, we will not discuss photoionization in condensed media,[3] although we will discuss collisional environments in the gas phase. In order to avoid confusion, let us decide to include sequential excitations through stationary intermediates (e.g. $A + h\nu \rightarrow A^*$; $A^* + h\nu \rightarrow A^+ + e$) under the umbrella of multiphoton ionization, even though many people would rather refer to such serial processes as 'multiple photon' ionization.

In Section II, several subjects of current interest will be discussed, and examples will be given in order to illustrate particular points. We do not intend to provide a historical summary of the development of MPI, since this would be terribly arduous and of questionable benefit in an area that is moving so quickly. Instead, we will focus on work which represents where the field is going and use examples from different research groups to punctuate our arguments. Every effort will be made to be critical and not simply act as a library retrieval service. In Section III, we will summarize what we believe are the most and least fruitful areas for future research, again trying to provide insight into a 'field' which is not really a field. In covering the literature as we have, it is inevitable that certain pieces of significant research are not referenced, when they should be. We extend in advance our apologies to parties who are thus slighted, and admit that our perspective reflects mainly our own interests, rather than a balanced overview of the whole subject.

II. RECENT RESULTS AND OBSERVATIONS

The pioneering work of Johnson and coworkers[4-9] and Dalby and coworkers[10-12] demonstrated conclusively that molecules could be efficiently ionized using MPI. This was a significant finding, since there was widespread fear at the time that molecules could not be pumped via multiphoton excitation to levels from which ionization could occur, because of access to
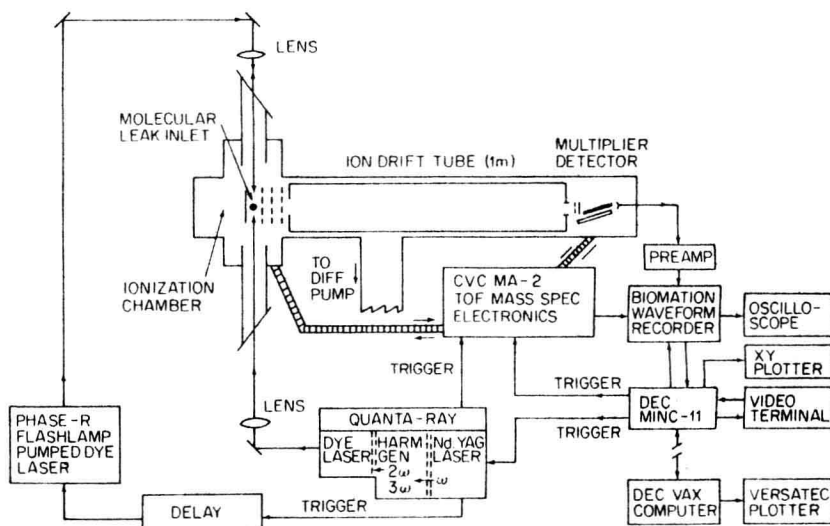
Fig. 1. Schematic diagram of the MPI apparatus used by Newton and Bernstein.[28] The phase-R dye laser pulse or electron ionization pulse could be triggered before or after the quanta-ray laser pulse.

dissociation channels at lower energies. Following these and other early contributions by several groups,[13-16] MPI developed momentum, receiving a major boost in the late 1970s and early 1980s due to experiments such as those from the research groups of Bernstein,[17-30] Smalley,[31-40] Schlag[41-48] and Zare.[49-53] By combining time-of-flight (TOF) mass analysis and computer-based data acquisition, they were able to accumulate data at an astounding rate. For groups which had previously worked at the technological frontiers of low S/N, it must have been gratifying to see entire mass spectra accumulate in < 1 s. Work in this area has continued at a very respectable pace until now, and it is appropriate at this time to take a hard look at MPI in order to soberly assess future prospects. The situation is similar in many ways to the 'discovery'
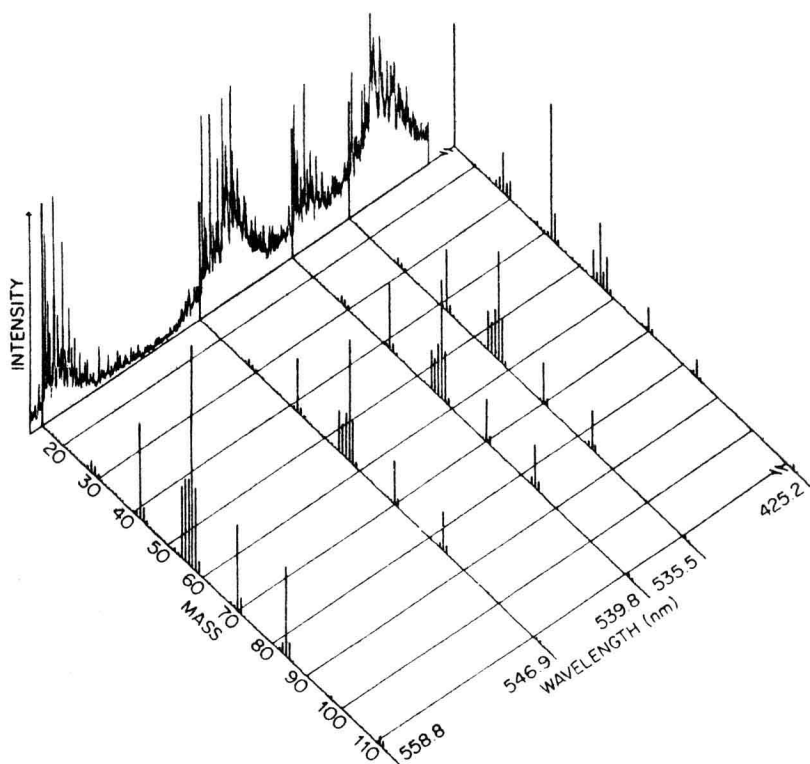
Fig. 2. Two-dimensional vibronic/mass spectrum of DABCO.[20] The 'back panel' gives essentially the total ion wavelength spectrum (actually the sum of the intensity of the principal ion 'clump' around $m/e = 57$); the 'stick diagrams' are digitized REMPI fragmentation patterns at the indicated laser wavelengths. The vertical line at the extreme left edge of each mass spectrum represents the sum of all the peaks shown in that spectrum, with a constant scaling factor throughout, except for that at 425.2 nm, where the entire spectrum has been scaled down by a factor of 10.

of infrared multiple photon excitation (IRMPE), in which a myriad of experimental observations were reported during a short period, but the more important research took some time to arrive.

Although it is possible in many instances to arrange conditions such that MPI leads predominantly to parent ions, this is not at all the rule. Fragmentation is often so severe that the ions produced do not resemble the starting material in any meaningful way. Using pulsed laser energies of several millijoules and focused laser beams, a complicated combination of excitation, fragmentation and ionization events lead to cracking patterns which depend
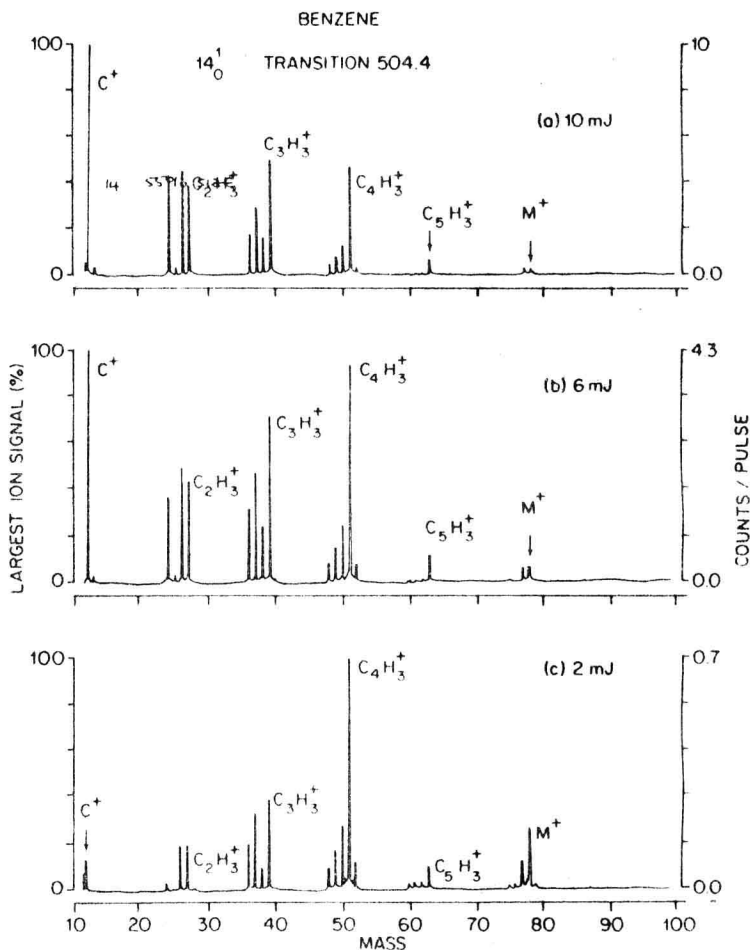

Fig. 3. The actual mass fragmentation patterns obtained for benzene of the 14^1 transition at the stated laser pulse energies.[29]

on both laser intensity and frequency. Several groups have tried to determine the pathways whereby ions are produced and the results are quite impressive for individual experiments.[17-30,54-60] However, there is little of a truly general nature which can be derived and one wonders if each case is not somewhat special. From conventional electron impact mass spectroscopy, we have learned that isolated electronically excited states of ions are the exception,[54-56] and therefore ions once formed will tend to fragment as per statistical theories.[61-65] The excitation/fragmentation of neutrals is more devious, and from the mass spectra alone it is hard to say whether the parent molecule dissociated and the fragments were then ionized or the ion was first produced and then fragmented.[66,67]

The work of Bernstein and coworkers[17-30] has provided massive amounts of information concerning intensity and wavelength-dependent fragmentation patterns of different types of molecules undergoing MPI. By developing a sophisticated computer controlled 'MPI machine', similar to that of Smalley's research group,[31-40] they were able to accumulate two-dimensional spectra (wavelength versus mass) at an enormous rate. The experimental arrangement is shown in Fig. 1 and typical data are shown in Fig. 2. One must bear in mind that data such as those shown in Fig. 2 were obtained with particular laser energies and that such two-dimensional spectra are therefore not unique. Examples of extreme cracking are shown in Figs. 3 to 5. In the case of benzene, C^+ is the dominant ion under conditions of high fluence, even though this species derives from the absorption of many photons, starting with C_6H_6. From the point of view of using MPI as a diagnostic tool, the intensity-dependent fragmentation is annoying, and the severe fragmentation at high fluence makes species identification impossible without a precise absorption signature.

The case of UF_6 is even more impressive.[68-70] In addition to U^+ being the dominant singly charged ion, the U^{2+} peak can be made as large as the U^+ peak[68] and U^{3+} is also detected (Fig. 6).[69] These highly charged species require that many photons are annihilated for their production, and Rhodes[71] has recently announced the MPI synthesis of highly charged uranium atoms which require ≥ 99 photons apiece for their manufacture. In sufficient concentration, these unique species could lead to coherent X-ray emission following charge transfer.

In scrutinizing the various cracking patterns, several groups[61-65] have pointed out that statistical treatments of the fragmentation which rely mainly on the information theoretic approach are in sensible accord with most observations. This is not surprising, in light of the tendency of ions to dissociate via ground electronic potential surfaces. Exceptions to the statistical distributions are not serious and are also of little significance because of the many experimental unknowns and the fact that there is no a priori reason to expect the distributions of fragments to be statistical. Thus, the information
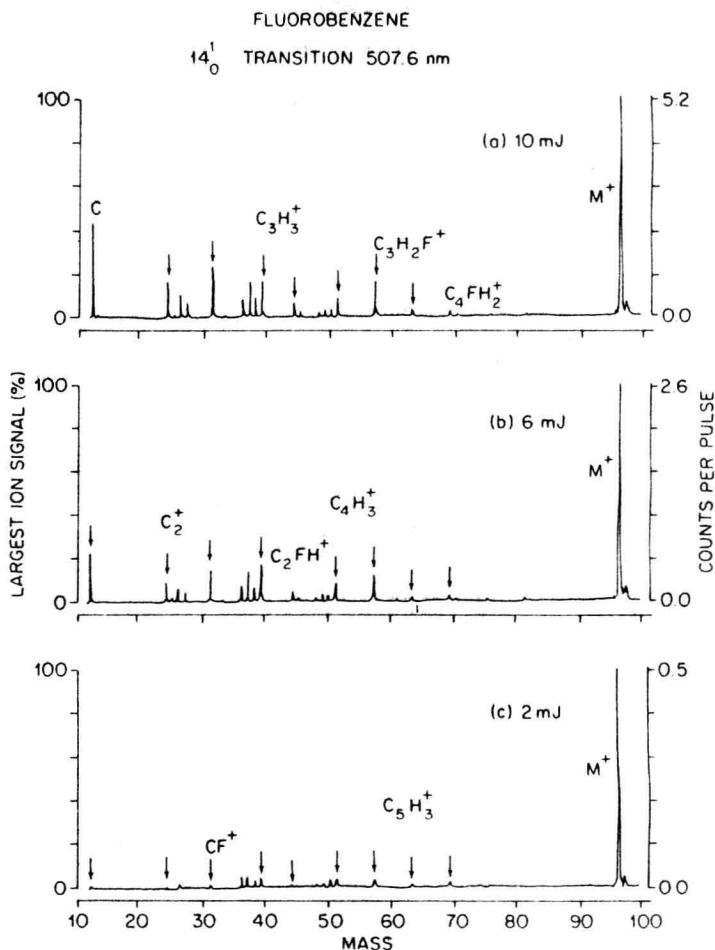
FLUOROBENZENE

14^1_0　TRANSITION　507.6 nm

Fig. 4. Actual mass fragmentation patterns obtained for fluorobenzene on the 14^1 transition at 507.6 nm at the stated laser pulse energies.[29] These mass spectra were obtained with a 0.25-m focal length lens at nominal ion gauge pressures of 5.0×10^{-5} torr.

theoretic approach provides a convenient means of cataloguing data and making educated guesses.

Smalley and coworkers [31-40] have pioneered many of the most elegant applications of MPI, wherein the method is used to prepare or analyse unique species and to probe molecular systems with exquisite detail. They showed that nearly 100 per cent ionization efficiency could be achieved with pulsed laser intensities $\sim 10^7$ W cm^{-2},[31] and were first to introduce the computer-
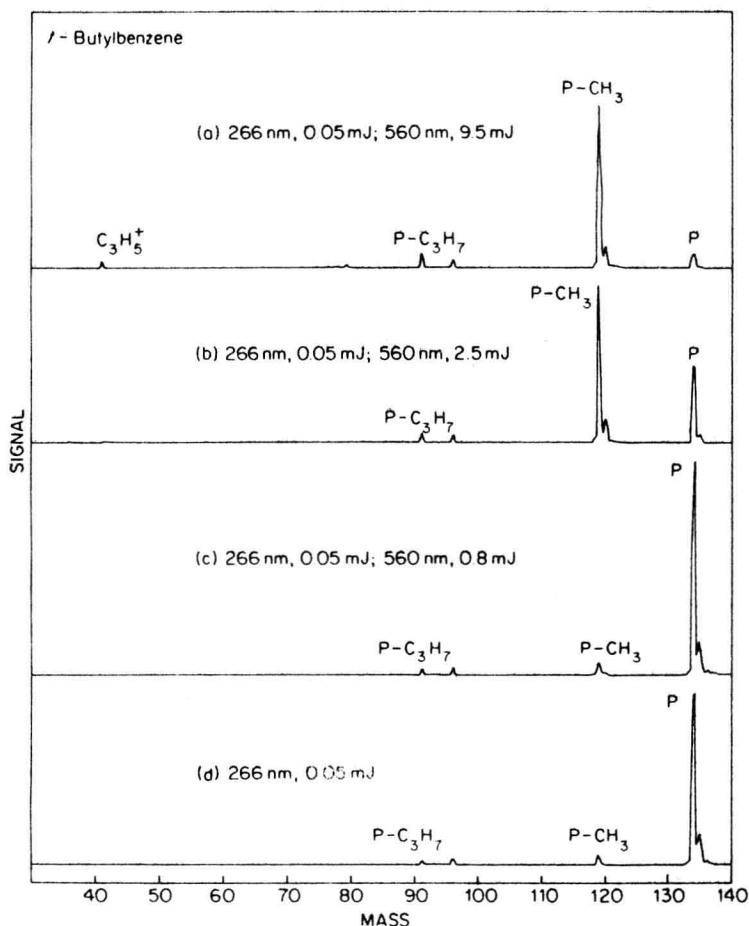
Fig. 5. Power dependence of two-colour fragmentation of tert-butylbenzene, showing the loss of a methyl group from the previously formed parent ion.[28] At the higher pulse energies several new fragments are seen to appear. Note the near complete destruction of the parent ion at the highest energy. The 'standard' MPI mass spectrum is shown in (d) for comparison.

controlled combination of TOF and free jet expansion technologies which has proven so invaluable in this area. They were also the first to use MPI for the detection of molecular triplets,[33,36,40] and by selectively exciting the $S_1(6^1)$ level of benzene, which undergoes intersystem crossing to the triplet, they were able to prepare vibrationally excited T_1, which subsequently decays to S_0 under completely collision-free conditions.[33] A partial energy level diagram indicating the relevant processes is shown in Fig. 7. Ionization from S_1 and/or
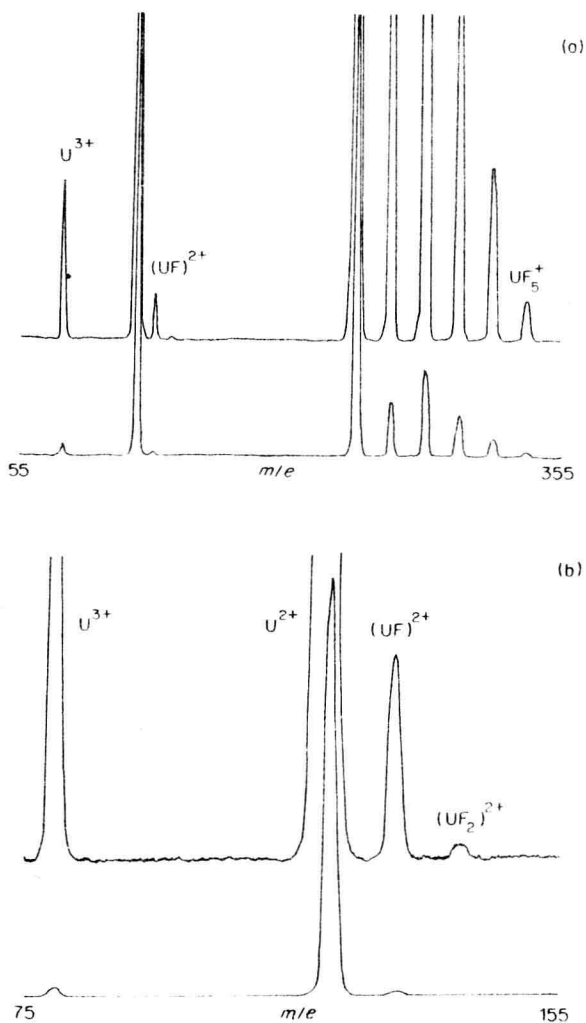
Fig. 6. MPI mass spectra following irradiation of UF_6 vapour with focused 266-nm radiation (10 mJ, 5 ns, $f = 200$ mm).[69] In (a), m/e in the range 55—355 is shown. The bottom scan shows the dominance of U^+ and U^{2+} in the mass spectrum. The upper scan ($\times$ 10 magnification) shows the smaller peaks more clearly. UF_6^+ was not detected. In (b), m/e in the range 75—155 is shown. Here, $(UF)^{2+}$ and $(UF_2)^{2+}$ are seen clearly, but there are no other detectable multiply charged molecular ions in the spectrum. U^+ is also absent.
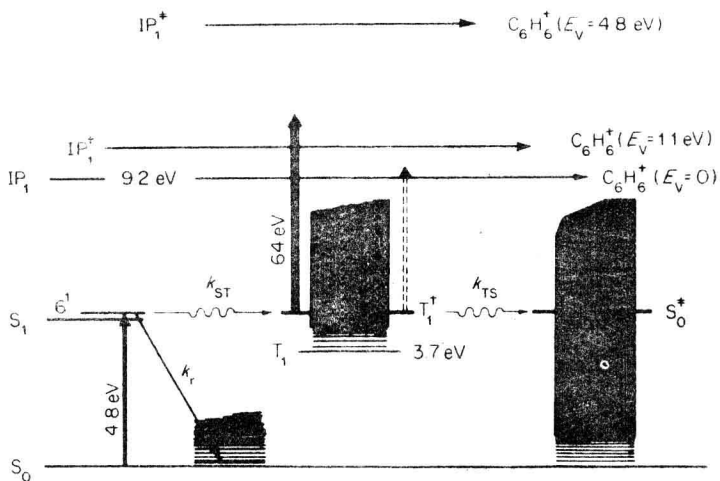
Fig. 7. Energy level diagram relevant to triplet detection by photoionization.[33] Dye laser radiation at 259 nm (4.8 eV) excites the cold benzene molecules to the 6^1 vibrational level of S_1 which then decays by fluorescence (at a rate k_f) and by intersystem crossing (at a rate k_{St}) to isoenergetic levels of the triplet manifold. The resultant vibrationally hot triplet, $T_1^\dagger$, then decays (at a slower rate, k_{TS}) into highly vibrationally excited ground state levels, $S_0^\dagger$. Franck–Condon factors for photoionizing transitions in benzene are vanishingly small unless the resultant $C_6H_6^+$ ion has the same vibrational excitation as the molecular state to be ionized. Thus, for the $T_1^\dagger$ hot triplet, only the ArF excimer laser radiation (6.4 eV) can produce efficient ion formation by exciting above the first ionization threshold $(IP_1^\dagger)$ which can produce $C_6H_6^+$ with 1.1 eV of vibrational energy.

T_1 is achieved with 193-nm radiation, and by scanning the delay between the excitation and probe lasers, the T_1 collision-free lifetime is obtained (470 $\pm$ 50 ns). Extensions to toluene,[36] pyrazine[40] and pyrimidine[40] underscore the generality of the method, and the utility of such precision measurements is evidenced in the discovery of the 'triplet lifetime mystery', in which triplets with more than a few thousand units of excess vibrational energy per centimetre decay many orders of magnitude faster than expected. In the threshold region, applied electric fields can influence ionization, just as for the case of atoms, and molecular Van der Waals clusters can be ionized softly enough to minimize fragmentation of the irradiated clusters (Figs. 8 and 9). Finally, Duncan, Dietz and Smalley,[35] discovered that metal clusters could be synthesized by irradiating microcrystals of metal carbonyls with 193 nm radiation (e.g. $[Fe(CO_5)]_n + h\nu(193\ nm) \rightarrow Fe_x$, $1 \leq x \leq 30)$, and they used the same radiation to ionize the metal clusters in a TOF mass spectrometer (Fig. 10). To date, this discovery has not been exploited, but it remains quite interesting nevertheless.
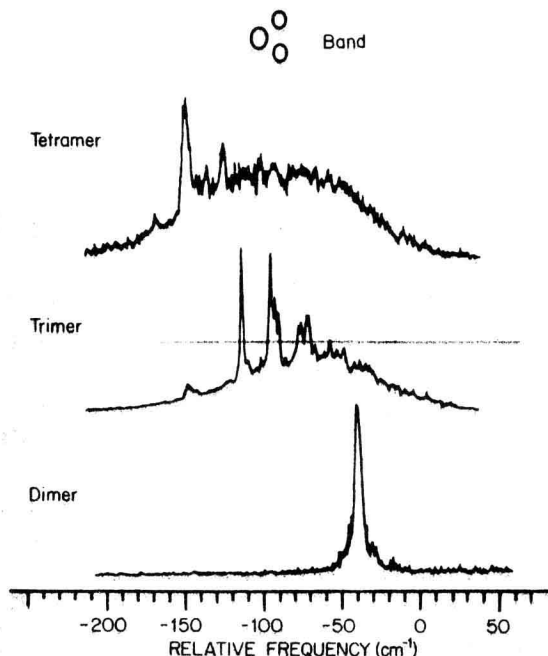
O^O_O Band

Fig. 8. Two-colour R2PI scan of the absorption bands of the
benzene dimer, trimer and tetramer in the region of the $^1B_{2u} (\pi\pi^*)$
$\leftarrow ^1A_g$ origin of benzene monomer.[38] The intensity for each
spectrum has been normalized here to a constant level. Actually,
the two-colour observed peak photoion signals were in the ratio
1:0.05:0.03 for dimer:trimer:tetramer respectively. The zero of
the relative frequency scale is set to the position of the forbidden
origin of the benzene monomer at 38 086.1 cm^{-1}. The red shifts of
the most prominent features from the monomer origin are —40,
—115 and —149 cm^{-1} for the dimer, trimer and tetramer
respectively. The strong features in the trimer spectrum centered
22 and 40 cm^{-1} to the blue of the origin are due to progression
activity in the Van der Waals modes of the cluster. Similar
features appear in the tetramer spectrum and constitute the main
observed optical phonon modes in the bulk benzene crystal.

A. Photoelectron Spectra Following MPI

Photoelectron spectra can help elucidate molecular electronic structure, as
well as the normal modes of molecular ions. Since the kinetic energies of the
ejected electrons reflect the Franck–Condon factors for the transitions under
consideration, data analyses are straightforward and complications arise
primarily because of poor resolution (~ 15 meV) and the selection rules
associated with the single step photoionization process. With MPI, resolution

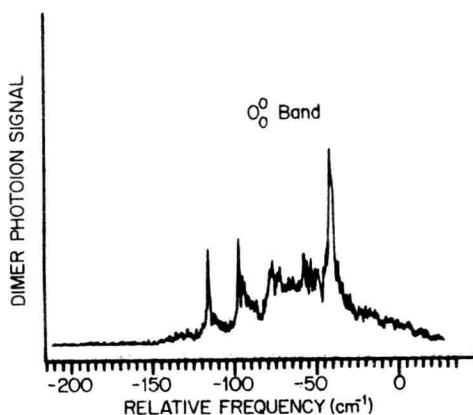**Fig. 9.** One-colour R2PI spectrum of the benzene cluster beam monitoring the photoion signal in the benzene dimer channel.[38] The frequency scale is relative to the monomer origin at 38 086.1 cm^{-1}. Note by comparison to Fig. 8 that most spectral features in this scan result from fragmentation of the trimer into the dimer signal channel.
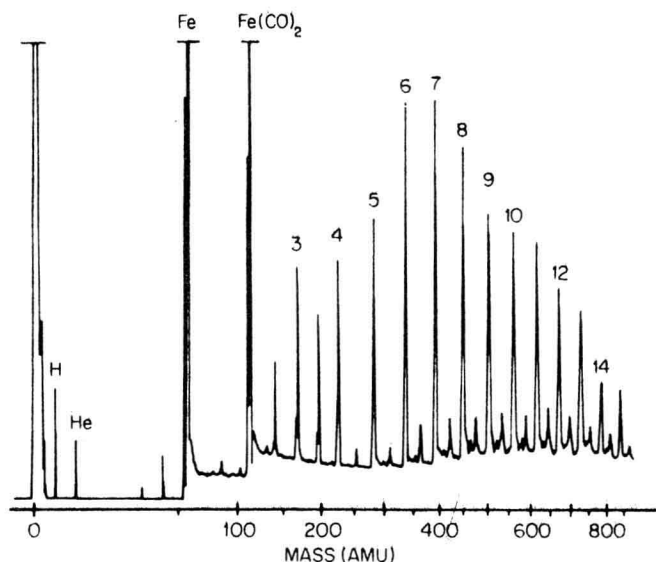

Fig. 10. Time-of-flight mass spectrum of ions produced by ArF laser excitation of a Fe(CO)$_5$ microcrystal beam.[35] Numbered peaks are predominantly due to bare iron clusters. Partially fragmented clusters of the type Fe$_x$(CO)$_y$, where y is odd, are seen as small peaks between the larger numbered features. Although these large peaks must contain some contribution from the even y clusters, there is no reason to expect a dominance of these even species in the partially fragmented distribution.