

Laser vaporization: A versatile method for studying metal clusters

V E BONDYBEY, I FISCHER and R SCHLACHTA

Institut für Physikalische Chemie der TU München, Lichtenbergstrasse 4, D-8046 Garching, Germany

Abstract. Vaporizing solid samples of metals and semiconductors with a YAG Laser is a method well suited for producing molecules and clusters of those materials. The clusters are examined by either laser-induced fluorescence (LIF) or mass spectroscopic methods. The technique is valuable for both gas phase and matrix studies. The method is described and some applications, studying either the structure of small metal molecules or their reactions, are reviewed, with emphasis on our recent results from the LIF studies of LiBe, Al₂ and the reaction of Al with oxygen, yielding Al₂O. For larger clusters, Ion Cyclotron Resonance is an extremely valuable method, as we demonstrate by its application to the reactions of small charged silicon clusters with strong oxidising agents.

Keywords. Laser vaporization; metal clusters; laser induced fluorescence; ion cyclotron resonance.

1. Introduction

Metal or semiconductor clusters or dimers, and other small, discrete molecules involving hard to vaporize, refractory solids are, under equilibrium conditions, difficult to generate in high concentrations, and studying them by classical spectroscopic techniques proved to be quite difficult. The first spectra of this type of molecules, Na₂ dimers date from the mid-19th century (Roscoe and Schuster 1874), but progress to other elements, beyond the alkali metals proved to be very slow.

The situation has changed rapidly in the recent years due to the development of novel techniques, among which, in particular, laser vaporization proved to be quite successful. The involvement of one of the authors with laser vaporization started at Bell Laboratories in 1973, and stemmed from the interest in multiply bonded silicon species, such as SiC or SiO₂. Since these molecules are not present in the equilibrium vapors above the solids, it was attempted to generate them by rapid, pulsed CO₂ laser vaporization. These experiments were inspired by the previous laser vaporization experiments by Leach and coworkers (Ohez *et al* 1969), but used a cold carrier gas to cool and quench the vaporization products. These were subsequently frozen in a low temperature matrix. IR studies of these matrices confirmed that the solids were successfully vaporized, but in the absence of isotopic data the interpretation of the complex spectra proved to be difficult (Bondybey and Bearder 1974).

The technique was resurrected several years later in our laboratory with the intent to study metal dimers and clusters. Using matrix isolation spectroscopy, we were able to clarify several controversies involving small metal clusters including Pb₂, Bi₂ and

* For correspondence

Bi_4 (Bondybey and English 1977, 1980) and we wanted to confirm these results in the gas phase by observing their laser induced fluorescence. This was immediately successful and in 1981 we reported gas phase LIF study of Pb_2 (Bondybey and English 1981, 1982), employing the laser vaporization technique. At the same time, the group of Smalley has reported the time-of-flight mass spectra of Al clusters generated in a similar way (Dietz *et al* 1981). Since then, the technique has proved to be generally useful in this type of study (Bondybey 1985), and is today in common use in numerous laboratories. Here we wish to concentrate on some of the results resulting from application of this technique in our laboratory.

2. Experimental details: laser vaporization

Unlike conventional experiments, where the sample is typically heated in a suitable furnace or container, in laser vaporization, a small volume of the sample itself is heated directly by the laser pulse. Since no container is required, the major source of contamination of the vapors is eliminated.

The vaporization process is rather complex. While the leading edge of the vaporization pulse is directly absorbed by the surface of the metal, a vaporized gaseous layer forms on a time scale, short when compared with the typical 10 ns duration of the pulse, and the trailing portion of the pulse may already be absorbed by the gaseous plasma.

The temperatures of the plasma – to the extent one can speak about equilibrium temperature – are very high. For most atoms the vapors are predominantly monatomic, and partially ionized. The ratio of ionized to neutral atoms, and the relative abundance of excited metastable atomic states are in many instances suggestive of temperatures in the range of 6000–8000 K.

A possible laser vaporization arrangement is shown in figure 1. The hot plasma is produced in a flow channel of a laser vaporization fixture, in the presence of a large excess of a cold carrier gas. The carrier gas, usually helium or argon can be at room temperature, or can be further cooled to 77 K by contact with a liquid nitrogen bath. The plasma is translationally rapidly cooled to the temperature of the carrier gas, and collisional processes can result in the formation of dimers and larger clusters. At the end of the flow channel, further cooling occurs as a result of an adiabatic expansion into an evacuated chamber. Depending on the system studied, both cooling mechanisms

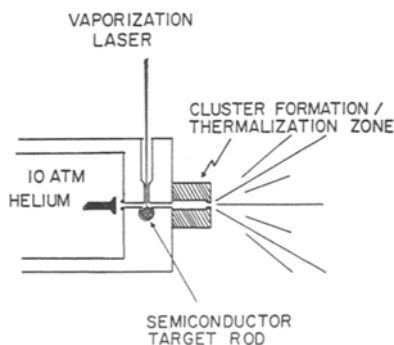
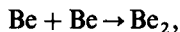


Figure 1. A typical laser vaporization arrangement, used in our laboratory.

have a useful function. The cooling of the gas in the flow channel is important for weakly bound species, whose bonding is comparable to room temperature kT values. Thus for instance for Be_2 , the equilibrium for the reaction:



lies at room temperature on the left hand side, and little or no diatomic products are observed. Cooling of the gaseous flow to 77 K shifts the equilibrium in favor of the associated product, and results in formation of copious amounts of Be_2 (Bondybey 1984; Bondybey and English 1984). The adiabatic expansion, on the other hand, results in dramatic cooling of the vaporization products into the range of several degrees K. This is for heavier or polyatomic species useful in simplifying their rotational spectra, but occurs too rapidly to permit significant formation of very weakly bound molecules not involving the carrier gas.

3. Experimental applications of laser vaporization

As noted in the title of the paper, the laser vaporization technique is very versatile, and can be conveniently applied in a large number of situations, wherever a source of cold atomic or molecular constituents of solid materials is needed. The great advantage of the technique is its generality – basically any solid, including the most refractory materials like tungsten, carbon, or silicon carbide can be vaporized. Indeed, the use of laser vaporization has spread in the last several years into virtually dozens of laboratories, and has been used for studies of chemical reactions, molecular dynamics, and in connection with about any type of spectroscopy.

In the present work, we will discuss two types of applications pursued in our own laboratories. Our early experiments were directed towards studies of LIF of metal or semiconductor clusters. Retrospectively, this proved to be less fruitful or general than originally hoped for. Absorption of a visible or UV photon brings many clusters above their dissociation limit, and in many instances fragmentation competes effectively with molecular fluorescence. Thus even in a number of metal dimers (e.g. Cr_2 or Ni_2) efficient predissociation was observed, and in polyatomic species this is more a rule than an exception. Furthermore, in clusters with more than a few atoms, nonradiative, “statistical limit” relaxation processes can occur even at energies below the fragmentation threshold. The LIF technique is, however, invaluable for studies of small, diatomic or triatomic species, where it gives detailed, accurate information about their geometry, molecular potential, and electronic and vibrational structures.

In the last few years heteronuclear dimers and clusters became a topic of increasing interest, which stems in part from the role of alloys as key industrial materials. The studies of such species by classical techniques are, however, difficult, and their properties are almost unknown. Laser vaporization is particularly useful in such molecules, which can easily be produced by vaporizing metal alloys (Bondybey *et al* 1983), or pellets formed by pressing mixtures of powdered pure metals.

The laser vaporization can also be used to produce negatively or positively charged cluster species. The advantage of ions is that they can be manipulated at will using electric or magnetic fields, and in this way trapped for virtually indefinite periods of time. We have used the technique to produce cluster ions of a variety of metal or semiconductor species (Reents and Bondybey 1986) and study their chemical reactions

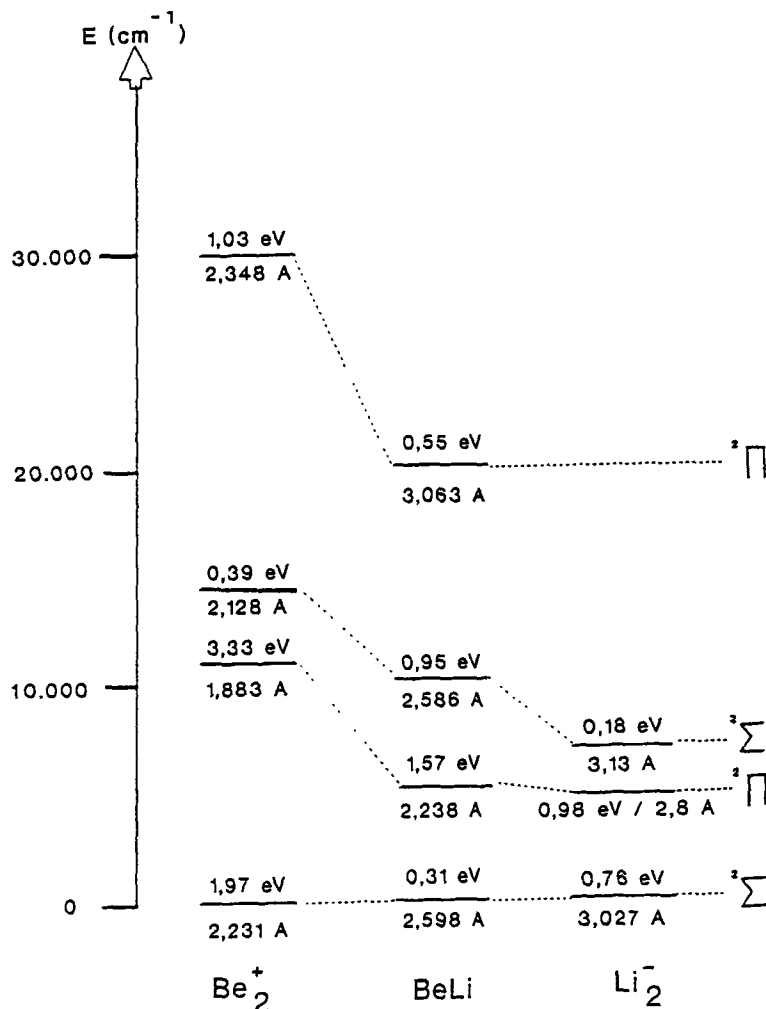


Figure 2. Comparison of LiBe with the isoelectronic ions Be_2^+ and Li_2^- . Values for Li_2^- are taken from Partridge *et al* (1983) and Michels *et al* (1985).

Table 1. Comparison of the spectroscopic constants of LiBe with the homonuclear dimers Be_2 and Li_2 (R_e in Å, k_e in N/m, all other values in cm^{-1}).

	Li_2	LiBe	Be_2
Bond order	1	1/2	0
D_e	8564	2480 ^a	790
R_e	2.67	2.59 ^b	2.45
$\Delta G_{1/2}$	346.2	295	223.4
B_0	0.669	0.637	0.609
k_e	25.5	20.2	20.2

^a Calculated value;

^b R_0 value

in an FT-ICR mass spectrometer. The disadvantage of such studies is the lack of direct structural information about the cluster species. An obvious advantage is the possibility of performing quantitative investigations of reaction rates and mechanisms of mass and charge selected clusters of basically any type of material.

In the following section, we give several representative examples of such studies in both areas, which contributed useful new results, and served to enhance our understanding of these interesting species.

4. Fluorescence studies of metal dimers

The analysis of rotationally resolved gas phase spectra of metal dimers can provide a useful insight into metal-metal bonding. We have concentrated on a variety of systems which were controversial either because of the disagreement between the experiment and theory, or where in spite of considerable theoretical interest and effort, no experimental data were available.

The successes of *ab initio* theoretical computations on the compounds of nonmetallic first row elements are quite impressive (Werner and Rosmus 1985), and the calculations rapidly approach spectroscopic accuracy. The situation for comparable metal containing systems is much less favorable. This is, at least in part, due to the lack of reliable experimental data to compare with the calculated properties and provide a guide to the further development of theoretical models.

The three simplest neutral metal clusters, Li_2 , LiBe and Be_2 , provide interesting examples. The three molecules contain 2, 3 and 4 bonding electrons, and the simplest molecular orbital theory predicts for them bond orders of 1, 1/2 and 0, respectively. The spectra of Li_2 (and of the other alkali metal dimers) are known and understood experimentally since the early days of spectroscopy (Loomis and Nusbaum 1931), and *ab initio* calculations predict their properties and spectra with amazing detail and accuracy (Jonsson *et al* 1981; Partridge *et al* 1983; Schmidt-Mink *et al* 1985; Kaldor 1990). For the other two species, Be_2 and the simplest heteronuclear cluster LiBe , on the other hand, there was up to rather recently (Harrison and Handy 1986; Røeggen *et al* 1987; Petersson and Shirley 1989) little agreement between the numerous theoretical works, and no experimental data existed. As recently as 1988, an extensive MR-CI calculation on LiBe predicted the ground state to be repulsive (Pewestorff *et al* 1988).

Using the laser vaporization technique, we were recently able to observe and analyze several electronic transitions of both molecules (Bondybey 1984; Schlachta *et al* 1990), and show that their ground states are bound. In table 1 we compare the experimental results on Be_2 and LiBe with those of Li_2 . The dissociation energies D_e decrease with the formal bond order as one would expect, but the bond lengths show the opposite effect. The Li dimer has the largest equilibrium separation R_e , and the Be dimer, whose dissociation energy is less than 10% of the value of Li_2 , the smallest R_e . This effect is undoubtedly due to the increased screened nuclear charge on Be and stronger binding of its electrons, but nevertheless is quite unusual. Also contrary to the usual expectations the force constants k_e of all three molecules are, in spite of the widely differing bond lengths and dissociation energies, of comparable magnitude. This unusual behavior shows that even our knowledge of the binding properties of the simplest molecules is still quite incomplete and a lot of interesting features can be found.

As a further test of our conclusions we have undertaken, in collaboration with P Rosmus, multi-reference CI calculations on BeLi (Fischer *et al* 1990). These clearly confirmed our conclusions and yielded a bound ground state with a dissociation energy of 0.31 eV. One of the most interesting features of the molecule is the unusual inverse anharmonicity in the $C^2\pi$ state resulting from an avoided crossing with the $A^2\pi$ state observed computationally and confirmed by the experiment.

Concurrently with LiBe we have examined also the isoelectronic ion Be_2^+ (Fischer *et al* 1990) whose spectra is thus far unknown. These results are compiled in figure 2 which compares the doublet states of the two molecules and of Li_2^- (Partridge *et al* 1983; Konawalow and Fish 1984; Michels *et al* 1985). The dissociation energies in eV and equilibrium bond lengths in Å are given explicitly, the excitation energies of the excited states can be estimated from the y -axis. The ordering of the states is the same in all molecules, and the trends in most physical properties are regular and monotonic. A notable exception is the dissociation energy which, although all three molecules have a formal bond order of 1/2, shows a rather pronounced minimum at LiBe. This can be probably be explained by the fact that the $2s$ orbitals of Li and Be are poorly matched energetically and overlap less effectively in the mixed species.

Cr_2 (Bondybey and English 1983) and Al_2 (Cai *et al* 1989a) are two other examples of molecules, where we succeeded in elucidating the symmetry and dissociation energy of the ground state. In Al_2 a previous experimental gas phase work was interpreted in terms of a $^3\Sigma_g$ ground state (Abe and Kolb 1983), while a matrix work (Douglas *et al* 1983a) concluded that it is of a $^1\Sigma_g$ symmetry. On the other hand, while earlier calculations seemed to support the gas phase result (Lamson and Messmer 1983; Upton 1986; Tse 1988) more recent works increasingly pointed to still other ground state, $^3\pi_u$ (Bauschlicher *et al* 1987; Sunil and Jordan 1988). Our techniques permitted the observation of several spectra, whose analysis confirmed the conclusions of these recent theoretical results. Whereas the main group dimers have been extensively studied in the last years, the dimers of the transition metals, especially the role of the d -electrons in the chemical bonding, are still a challenging problem for experimentalists and theoreticians. Cr_2 is a prototypical of this type of molecule. We were recently able to observe the laser induced fluorescence of this molecule, and deduce its vibrational and rotational constants (Bondybey and English 1983). While the extremely short bond length of 1.67 Å and a high value of ground state vibrational frequency, $\Delta G_{1/2} = 451 \text{ cm}^{-1}$ are consistent with the formal bond order of 6 of the $^1\Sigma_g$ ground state, the binding energy is relatively low. It should be noted that for the Cr dimer still no quite satisfactory *ab initio* results are available.

5. Studies of metal atom and cluster reactions

The laser vaporization is also valuable for studying chemical gas phase reactions and reaction products. For example, by reacting metal atoms with organic halides, cold metal halides and organic radicals can be produced and experimentally studied. This we have recently exemplified by the reaction of Ba with benzyl chloride to produce adiabatically cooled benzyl radicals (Cai *et al* 1989b). Similarly, by entraining in the carrier gas N_2O , oxygen or other reactive gases, metal oxides, hydrides, carbides or nitrides can easily be studied. For instance, we were able to record spectra of the diatomic hydride, carbide, nitride and oxide of Pd (Bondybey, unpublished results).

Among the most important industrial chemical reactions are metal oxidation and reduction. Whereas the monoxides of most metals were rather extensively studied, much less information is available about molecules containing more than one metal atom due to the difficulty in generating them and the complexity of their spectra. Very recently we have studied the oxidation of Al atoms and clusters produced by laser vaporization with oxygen and have detected, in addition to the diatomic AlO oxide, Al₂O also (Cai *et al* 1990). Although this most stable high temperature oxide of aluminum has been studied quite extensively (Linevsky 1961; Buchler *et al* 1963; Snelson 1970; Makowiecki *et al* 1971; Knight and Weltner 1971; Sonchik *et al* 1983; Douglas *et al* 1983b), its properties are still controversial, and no consensus exists as to its molecular structure. A part of its vibrationally resolved spectra is shown in figure 3.

Our wavelength resolved emission spectra show rather clearly that the molecule is linear and centrosymmetric both in the ground state and in the upper state of the observed transition, with a rather low value of bending frequency, very similar to the isoelectronic C₃ radical. The observed vibrational frequencies of 525, 99 and 993 cm⁻¹ for ν_1 , ν_2 and ν_3 show very good agreement with recent theoretical predictions (Wagner 1974; Masip *et al* 1988), as can be seen from table 2. The examination of the excited state is much more complicated. It seems to be of π symmetry, so one can expect a large Renner–Teller effect, as in the corresponding state of the isoelectronic C₃. In

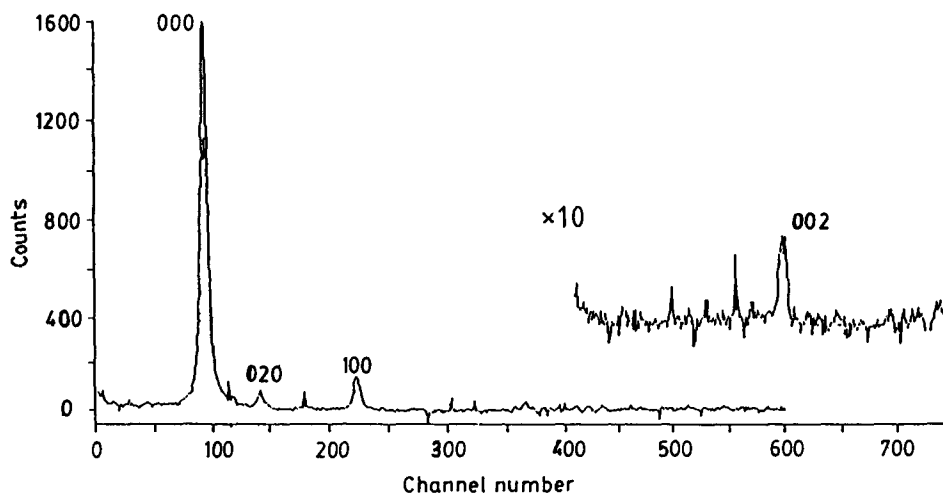


Figure 3. Part of the electronic spectrum of Al₂O.

Table 2. Comparison of the observed vibrational frequencies of Al₂O with theoretical calculations (all values in cm⁻¹).

	ν_1	ν_2	ν_3
Experiment	525	99	993
Wagner (1974)	527	102	1057
Masip <i>et al</i> (1988)	531	129	1012

addition it seems to be strongly perturbed by another electronic state. Further experiments have to be done for a meaningful analysis of this state.

6. Matrix trapping of laser vaporized species

The laser vaporization can be conveniently combined with matrix isolation to provide a useful source of trapped clusters and high temperature molecules for spectroscopic studies (Heimbrook *et al* 1987). The same pulsed valve and vaporization fixture employed in the gas phase experiments can be used, simply by replacing helium with a condensable carrier gas like Ar, Ne and freezing the adiabatically cooled products on a cold matrix substrate. Such a technique has considerable advantages compared with conventional matrix methods. It minimizes the chances of sample contamination by reactions with impurities or surface walls, and maximizes the amount of cluster products, since, unlike in a conventional matrix experiments, they are formed already prior to deposition, in the vaporization fixture. The species studied by this technique in our laboratory range from metal atoms (Ca, Mo³⁰, Ni) (Heimbrook *et al* 1987a; Rasanen *et al* 1987a) and dimers (Ca₂, Pb₂, Mo₂), oxides (PbO) (Heimbrook *et al* 1987), SiC₂ (Bondybey 1982a) and C₃ (Bondybey and English 1978) radicals and the C₂⁺, C₂ and C₂⁻ species (Rasanen *et al* 1978b). While in some areas the matrix isolation method has been supplanted by new techniques, in particular by the supersonic jets, in other respects it continues to be an extremely viable and valuable technique. It permits the accumulation of the products over thousands of vaporization pulses and stabilization of high concentrations of products. It is also easy to search wide spectral regions. It is therefore invaluable in preliminary location and searches for electronic transitions of species whose spectroscopy is unknown. Thus we were able to observe in this way for the first time the electronic absorption spectrum of C₂⁺. The matrix work has shown that this important molecular ion has a quartet ground state, in agreement with the theoretical calculations of Rosmus (Rosmus *et al* 1986), and contrary to previous report of the observation of a doublet-doublet transition (Meinel 1972).

The technique is also very well suited for study of electronic states, which due to the spectroscopic selection rules, cannot be directly excited from the ground state in a gas phase experiment. One can take advantage of the fact that the selection rules are often relaxed in the matrix to access the excited state directly. Alternatively, one can excite the molecule into a higher lying electronic states or into the dissociative continuum, and rely on relaxation phenomena such as cage recombination and electronic and vibrational relaxation to access the desired state. This is exemplified by our studies of matrix isolated Cu₂ (Gole *et al* 1982; Bondybey 1982b), Mo₂ (Kundig *et al* 1975; Klotzbücher and Ozin 1978; Moskovits *et al* 1985), or of the homonuclear and heteronuclear group V dimers (Bondybey 1989).

As noted, a fundamental limitation of LIF studies is due to the vanishingly small fluorescence quantum yields of some clusters, as demonstrated for example in the case of Ni₂ (Rasanen *et al* 1987). The rates of competing nonradiative processes should decrease with decreasing densities of molecular states. One might therefore expect the emission from low-lying excited electronic states of many dimers and larger clusters to be observable in the red and infrared regions, as observed for instance in Cu₂, Mo₂. Similar emissions from many other cluster species could undoubtedly be observable

using IR-detectors. Most of the cluster species contain strong absorptions in the visible or near-UV, permitting very efficient pumping using tunable dye lasers. In our future work we want to search for such IR-emission following visible or UV excitation, with the help of a Fourier transform IR-spectrometer.

7. FT-ICR studies of ionized metal and semiconductor clusters

As noted above, laser vaporization generates, besides neutral atoms and clusters, also abundant ionic species. These can be studied conveniently by FT-ICR techniques. The disadvantage of such mass spectroscopic studies is the lack of direct structural information. The advantage is that their application is not dependent upon the existence of stable excited electronic states, and they can provide a useful comparative information about the rates and pathways of metal atom and cluster reactions.

Metal or semiconductor cluster ions are created by laser evaporation of a bulk target rod located outside the ion cell of a modified Nicolet FT-MS-1000 Fourier transform mass spectrometer (Mandich *et al* 1987). The ions are confined axially by an electric field and radially by a strong magnetic field. In this way, they are constrained to move on spiral trajectories, with ion cyclotron resonance frequencies characteristic for their mass/charge ratios. In this way, the ions can be trapped for long periods of time (typically periods of seconds to minutes) and their chemical reactions conveniently studied.

As an example, we have studied the reactions of both negatively and positively charged clusters of carbon, silicon and several III-V semiconductor species. Silicon clusters have been reacted with methylsilane (Mandich *et al* 1986), nitrogen dioxide (Mandich *et al* 1987), tungstenhexafluoride and xenon difluoride (Reents *et al* 1986). Quite interesting are the oxidations of silicon clusters with various strong oxidizers,

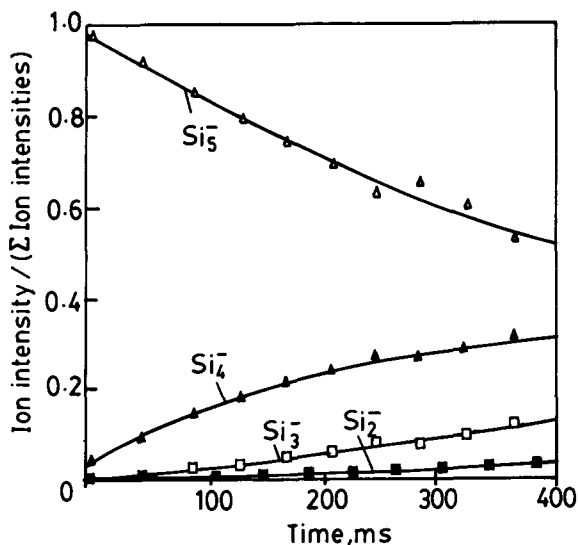
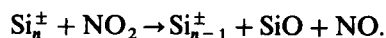


Figure 4. Time evolution of product formation in the reaction of Si_5^- with NO_2 (9×10^{-10} torr). Product intensities have been corrected for isotopic abundance and normalized to the total ion intensity of the cell.

such as NO_2 , XeF_2 , ClF_3 and others. For instance, reactions with nitric oxide remove in a stepwise manner Si atoms from the surface of the cluster:



These reactions, which are quite reminiscent of reactive plasma etching of silicon surface can thus be studied in microscopic detail as a function of cluster charge and size of the Si atoms.

Figure 4 shows the time evaluation of the formation of small Si^- cluster in the reaction of Si_5^- with NO_2 . The product intensities are corrected for isotopic abundance and normalized to the total ion intensity of the cell. The curvature of product formation indicates that Si_4^- is a primary product whereas the smaller molecules are higher order products.

8. Summary

It is shown that laser vaporization is a versatile method for all kinds of experiments involving metals, alloys and semiconductor molecules and clusters. The combination with LIF studies proved to be very helpful in elucidating the binding properties of small molecules, both homo- and heteronuclear. Our recent results on LiBe, which was calculated to be unbound in the ground state, show that even our knowledge of small metal containing molecules is still incomplete. The method is also applicable for studying the chemical reactions of those molecules. A recent example is the formation of Al_2O , examined in our laboratory. For larger clusters, where LIF is not applicable, ICR is a convenient alternative. With its high mass resolution and long retention times it provides an excellent route to the examination of metal clusters of any size. Its advantages are exemplified by its application to the reaction of charged silicon clusters with NO_2 , demonstrating a stepwise "etching" and loss of Si atoms.

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