Vol.13 No.3 NUCLEAR SCIENCE AND TECHNIQUES August 2002

Collision of low energy Na^+ ion with C_{60}

ZHANG Jian-Guo

(*Naval Medical Research Institute, Shanghai 200433*)

GONG Jin-Long, LIN Sen-Hao

(*Shanghai Institute of Nuclear Research, the Chinese Academy of Sciences, Shanghai 201800*)

Abstract The collision-induced reaction of Na^+ ion with neutral C_{60} vapour was investigated at the energy range of 10 to 150 eV. The deposited films were studied via laser desorption time-of-flight mass spectroscopy (TOFMS). The fragment products of C_{60} with even number of carbon atoms, such as C_n^+ (n=58, 56, 54), and adduct products, such as C_n^+ (n=62, 64, 66, 68) were observed in the positively charged TOF mass spectra. The endohedral fullerene ion of $Na@C_{60}^+$ was detected when collision energies are above 20 eV. Besides, no negative endohedral fullerene was detected, the products appearing in positively charged mass spectra were also observed in the negatively charged mass spectra. In addition, a series of products with odd number of carbon atoms, such as C_n^- (n=53, 55, 57, 59, 61, 63, 65, 67), also appeared, but the intensities of their signals were not as high as that of even numbered. Finally, it is interesting to find that the deposited films are insoluable in toluene, benzene or water. Their Fourier transform infrared (FTIR) spectra seem like those photopolymerized ones. Some of the reaction schemes are proposed to explain the experimental results.

Keywords C_{60}, Carbon cluster, Endohedral fullerene, Ion collision, TOF mass spectra

CLC numbers O484.5, O561.4, O562.4, O657.63 A

1 INTRODUCTION

Collision between C_{60} and a variety of ions or atoms are becoming now a new branch of cluster research. The aim is to gain better understanding of the behavior of this novel material, not only for theoretical investigation, but also for future applications. It is possible to form new compounds when atomic or molecular substituents are attached to C_{60} cage surface, or when carbon atoms in the cage are replaced or displaced by ejective ions. On the other hand, the cavity in C_{60} with diameter of ~0.55 nm is large enough to trap an atom or small molecule inside[1], or even the cage will open a window to form an endohedral site for containing an atom, which may or may not be bound to the interior surface of the C_{60} cage.[2]

Weiske *et al.*[3] and Ross and Callahan[4] suggested that $He@C_{60}^+$ endohedral complex formed in C_{60}^++helium collisions at energies of tens electronvolts. $M@C_{60}$ denotes

---

Manuscript received date: 2000-01-14

M (ion) metal inside the C_{60} cavity. This conclusion has been confirmed by further experiments from both groups which support an endohedral structure for the complex.[5,6] Campbell *et al.*[7] studied the collision energy dependence of C_{60}^++Ne ion collisions and observed that the appearance energy is about 9 eV for Ne@C_{60}^+. Kleiser *et al.*[8] first reported that He atom could be captured by negatively charged C_{60}. By using a mass-selected ion beam of guided-ion beam tandem mass spectrometer, Wan *et al.* reported their results of threshold energy in Ne^++C_{60} reaction[9]. It is interesting to find that different threshold energies were reported for the collision systems of C_{60}^++Ne(9eV)[7] and Ne^++C_{60}(~20 eV).[9] Anderson's group reported systematic studies of endohedral complex formation and fragmentation in M^++C_{60}/C_{70} (M=Li, Na and K) system.[10,11] The insertion of Li^+ and Na^+ to form the endohedral $[Li@C_{60}]^+$ and $[Na@C_{60}]^+$. These species were observed at appearance energies of ~6 and ~18 eV, respectively. They also published brief reports on the chemistry of C^+[12], O^+[13] and N^+[14] ion collision with C_{60}. Recently, Tellgmann and co-wokers[15] reported that when monolayers of C_{60} film exposed to an intense beam of Li^+ ion of 30 eV kinetic energy, about 27% of the alkali-containing endohedral C_{60} were produced.

In this paper we present some of the new results on the collision of C_{60} neutral vapour with Na^+ ion beam, which was generated from a solid ion source. Mass-to-charge ratio (m/z) of the deposited film was measured with a TOFMS. In addition to the expected Na@C_{60}^+ endohedral fullerene, we also obtained odd numbered clusters of C_{55}, C_{57}, C_{59}, C_{61}, C_{63}, etc., in the negatively charged mass spectrum. Similar to photochemical polymerized fullerene, it is found that the deposited film is toluene insoluble and believed to be a polymer.

2 EXPERIMENTAL

Home made C_{60} powder with a purity higher than 99.5% was used in this experiment as a deposition source after baking a vacuum of 10^{-4} Pa at 573–673 K for 10 minutes and then at 523 K for a few hours to remove solvent. The neutral C_{60} vapour was generated from an oven, which was made of a brass cylinder with a small hole. The substrate of silicon wafer was set in the vacuum chamber. The ion beam was produced from thermionic emission of a special solid alkali ion source provided by SPECTRA-MAT, Inc., USA. Through a simply designed accelerator and Einzel lens, the ion beam was accelerated from 10 eV to 150 eV, which could be changeable continuously. The beam current could be as high as 2 μA and was measured with an integrated circuit meter. By simultaneously heating both C_{60} (about 623 K) and ion source under 10^{-4} Pa, the collision of Na^+ ion and C_{60} vapour was carried out just before the deposition and in front of the substrate surface. Collision products were deposited on the silicon substrate and then kept in the vacuum chamber for measurement later. The deposition rate of C_{60} vapour was about 0.1 nm/s, which was monitored by a quartz-crystal thickness meter, and the flux ratio between C_{60} and ion beam was about 1:1. The typical thickness of the film was about 300 nm.

Mass analysis is done with a laser desorption time-of-flight mass spectrometer (TOFMS). Argon ion laser (488 or 514 nm) was used to produce plasma, which has a pulse width of 5ns and a power of 15 W/cm^2. Both positive charged and negative charged ions could be generated and detected by the TOFMS.

3 RESULTS AND DISCUSSION

3.1 Positively-charged ion spectrum

When the Na^+ ion collision with neutral C_{60} vapour at the impact energy 40 eV, the positive charged ion spectrum is shown in Fig.1a, which shows the distribution of the fullerene cations from C_{54}^+ to C_{70}^+, while Fig.1b shows the details of the neighborhood of the m/z=744. Multiple peaks in each m/z are due to the presence of the ^{13}C isotope. At low collision energies, the spectra show that the dominant product is C_{60}^+, in part resulted from charge transfer reaction and in part resulted from the laser desorption of the neutral C_{60}, with which the collision has not happened. It is found the endohedral fullerene product of $Na@C_{60}^+$ is presented obviously. The spectra show that there is no evidence of any significant intensity for fragment products (e.g. C_{58}, C_{56}) or substitutional products (e.g. $C_{59}Na^+$). From Fig.2 we can see that the $Na@C_{60}^+$ ions appears above ~20 eV. This behavior is much similar to the results of Anderson.[9] They observed the insertion of the Na^+ to form endohedral fullerene species of $Na@C_{60}^+$ with the appearance energy of ~18 eV. The relative intensity of the peak rises rapidly, as the impact energy is increased. At the same time the fragment products, such as C_{56}, C_{58}, and the higher mass products, such as C_{62}, C_{64}, appears gradually. The $Na@C_{60}^+$ signal reaches the highest around the collision energy of ~50 eV. Further increase in collision energy, the intensity of $Na@C_{60}^+$ signal is decreased gradually. Higher mass products disappeared as collision energy exceeded ~60 eV. With higher resolution and sensitivity, still no substitutional products, such as $C_{59}Na^+$, or higher mass adduct products, such as NaC_{62}^+, NaC_{64}^+ were observed.

The dominant products in the spectrum is the contribution from C_{60}^+. In all cases, charge transfer reaction is endoergic reaction:

$$Na^+ + C_{60} \longrightarrow C_{60}^+ + Na \qquad \Delta H = 2.47\,eV$$

Where ionization potential (IE) of C_{60} is taken to be 7.61 eV. It seems that it is not reasonable to consider the charge transfer reaction being responsible for the low energy C_{60}^+ production. But at higher collision energy, C_{60}^+ is affirmatively the dominant product from charge transfer reaction. The product of C_{60}^+ is also available in C_2^+ induced charge transfer reaction:

$$C_2^+ + C_{60} \longrightarrow C_{60}^+ + C_2 \quad \Delta H = -4.52\,eV$$

This exoergic reaction is entirely possible even at low collision energies, which cause the presentation of the adducts formation, such as C_{62}^+, C_{64}^+. As the collision energy is increased above 60 eV, these adducts products disappeared, and are replaced by a series of C_{60-2n}^+ products.

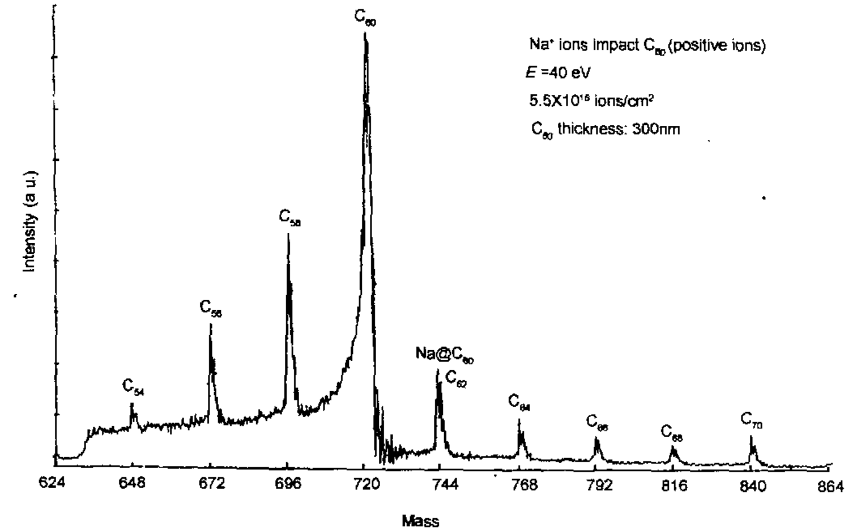

Fig.1a Time-of-flight mass spectrum of positively-charged ions, showing the distribution of the fullerene cations

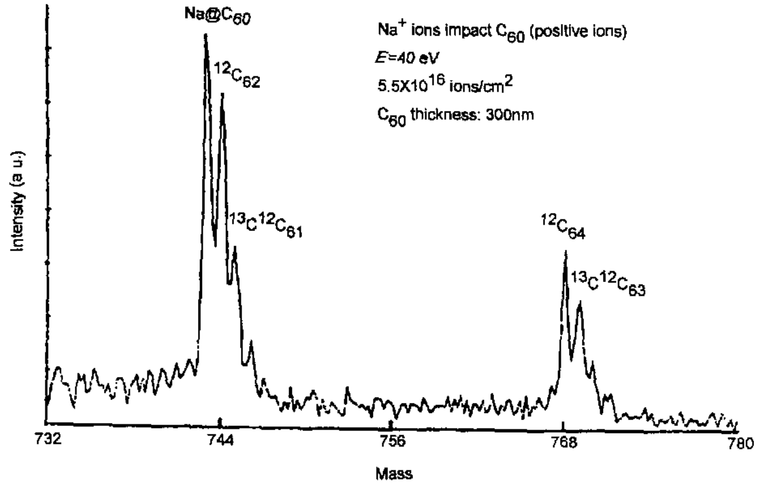

Fig.1b Time-of-flight mass spectrum of positively-charged ions, showing the detail of the neighbouhood of endohedral $Na@C_{60}^+$

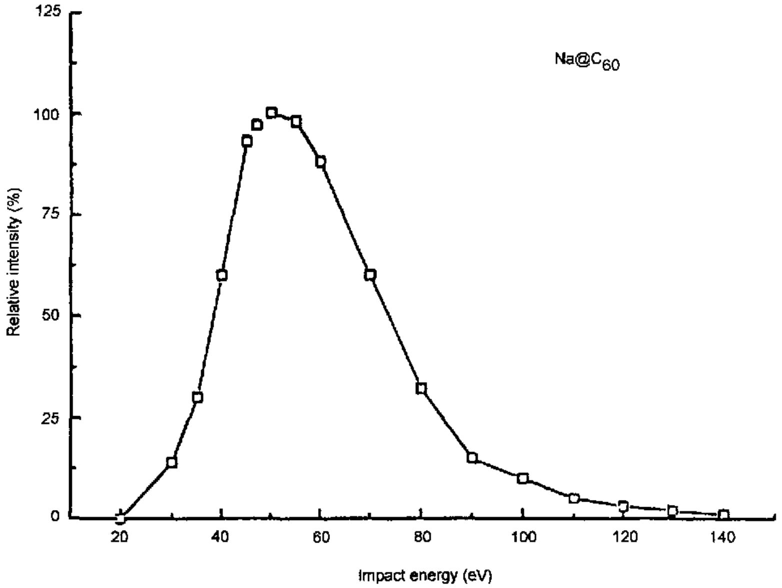

Fig.2 Dependence of the output of the endohedral fullerene Na@C$_{60}^{+}$ with collision energy

The endohedral fullerene of Na@C$_{60}^{+}$ is clearly observed in Fig.1a and Fig.1b. It is well known that C$_{60}$ molecule consists of 60 carbon atoms, connecting each other with single C-C bond or double C=C bond. The bond length for 6–6 double bond and 5–6 single bond are 0.140 nm and 0.145 nm, respectively. The 6–6 bond is harder to open because it is shorter at equilibrium. The ionic radius of Na^{+} is ~0.12 nm, slightly larger than the radius of 6-membered ring. According to theoretical calculation[2] of a C$_{60}$ "window" mechanism, a large 9-membered ring could be opened with 0.248 nm in diameter by breaking a 5–6 bond on C$_{60}$, through which an atom or small molecule may pass. It is reasonable to suggest that energetic Na^{+} ions would be able to open such window by energy transfer. Consequently, the Na^{+} ion is caught into a fullerene cage, producing a Na@C$_{60}^{+}$ endohedral compound. Recently, *ab initio* molecular dynamics simulations[16] came to a similar conclusion that the bond breaking after the bombardment may make the insertion of Na^{+} ion easier and after the insertion of Na^{+} ions through the largely opened hole, the original C$_{60}$ cage is reconstructed after annealing. We also observed the usual series of C$_{60-2n}^{+}$ fragmentation products. This is presumed that some amounts of the collision energy is transferred to the C$_{60}^{+}$ product and changed it to the excited state. When deexcited, the decomposition products were obtained:

$$\mathrm{Na^{+} + C_{60} \longrightarrow C_{60}^{+*} + Na \longrightarrow C_{60-2n}^{+} + nC_2 + Na} \quad (n = 1, 2, \cdots)$$

This pattern of fragmentation is usually observed in all M^{+} + C_{60} collision system.

It was somewhat surprising that no decomposition reactions, such as the series of C_2-loss products

$$Na@C_{60}^+ \longrightarrow Na@C_{60-2n}^+ + nC_2 \quad (n = 1, 2, \cdots)$$

were observed in Na^++C_{60} system. Anderson reported that at higher collision energies, the hot $[Na@C_{60}]^+$ appears to relax by losing C_2 units and yielding $[Na@C_{60-2n}]^+$. It is presumed that the lifetimes of the series of metastable fragment products of $[Na@C_{60-2n}]^+$ are not long enough to be detected in our case.

3.2 Negatively-charged ion spectrum

In order to elucidate the reaction scheme, the negatively-charged time-of flight mass spectra were obtained in the same collision energy range. From Fig.3 we can see the distribution of negatively-charged carbon cluster ions. Besides the distribution of even numbered carbon clusters (C_n^-: n=54, 56, 58, 60 etc.) appeared as usual, the distribution of odd numbered carbon clusters (C_n^-: n=53, 55, 57, 59 etc.) were obtained, although the intensities of odd numbered clusters were significantly reduced relative to that observed for the even numbered. Also multiple peaks in each m/z are due to the presence of the ^{13}C isotope. Similar results have been observed in our previous experiments of the C_{60} film impacted with high energy K^+ ion beam.[17] In contrast to the behavior of the positively-charged spectrum, it is quite strange that why there is no detectable contribution from endohedral fullerene to adduct products in the negatively-charged spectra of TOF, and why the odd magic number was only observed in the negatively-charged collision products.

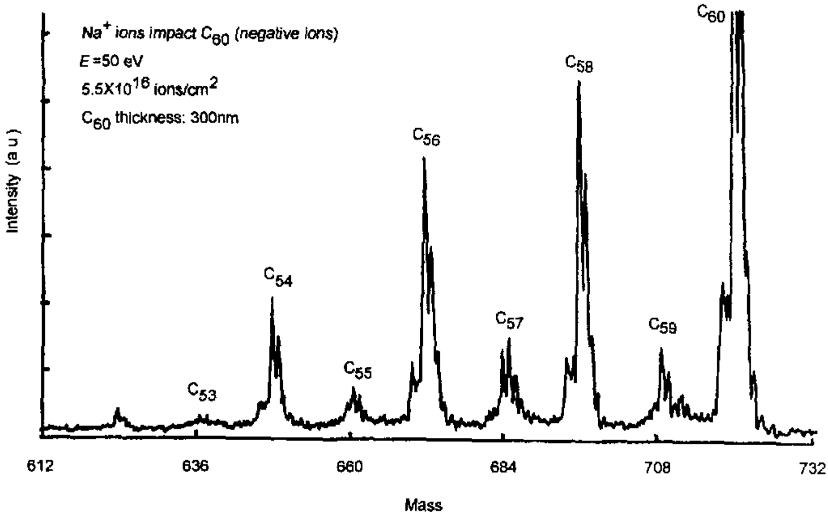

Fig.3 Time-of-flight mass spectrum of negatively-charged ions, showing the occurance of odd numbered C_n^- (n=55,57,59,61,63)

To simplify the analysis, we designed our experiment to allow observation of the negatively-charged ions formed only within the C_{60} deposition film in the same experimental apparatus without the collision of Na^+ ion beam. The spectrum shows that the distribution is nearly identical to that measured previously from positively charged ion laser desorption time-of-flight mass spectra and no odd numbered carbon cluster has been observed. This suggests that the appearance of odd numbered carbon cluster in negatively-charged spectrum does not result from the laser desorption, but more probably from the bombardment of Na^+ ions. This negatively-charged spectrum was postulated to result from the contribution of fragment products (e.g. C_{58}^-, C_{56}^-, etc.) and substitutional products (e.g. $C_{59}Na^-$), simultaneously. The behaviour of fragment products is almost the same as that in the positively-charged spectrum. While these substitutional products are metastable and sequentially dissociated by the loss of Na and C_2:

$$C_{59}Na^{-*} \longrightarrow C_{59-2n}^- + nC_2 + Na \quad (n = 0, 1, 2, \cdots)$$

The long lifetimes of charge transfer ion/molecule collision allows for geometric changes from a not so stable ionic cluster structure to the more stable neutral structure, which is detectable in the TOF spectra. It seems that the substitutional reaction in negatively-charged situation is easier to emerge than in positively-charged. Since a carbon atom is so small, the average nearest neighboring C-C bond on the C_{60} surface is only 0.143 nm, and the ionic radius of sodium atom is 0.12 nm. Therefore, Na^+ can be expected to substitute for a carbon atom on the C_{60} cage surface. We speculated this could in part explain why only the odd numbered clusters were observed in negatively-charged mass spectra.

3.3 Soluability and polymerization

It is well known that the pristine C_{60} is soluable in toluene to produce a purple liquid. When we try the soluability in toluene, benzene or water for the C_{60} deposition film after impacted with Na^+ ion beam, it has been found insoluable after immersed for several days. TOF spectra and Fourier transform infrared (FTIR) transmission spectra of pristine C_{60} film and that impacted with Na^+ ions were carried out to compare their differences. There are no obviously differences in the TOF spectra. For FTIR studies, films (~300 nm) were deposited on KBr substrates. Fig.4 shows a typical FTIR spectrum at room temperature. Group theory for an isolated C_{60} molecule predicts that four ($4F_{1u}$) lines ($F_{1u}(1)$, 527.1 cm^{-1}; $F_{1u}(2)$, 570.3 cm^{-1}; $F_{1u}(3)$, 1169.1 cm^{-1}; $F_{1u}(4)$, 1406.9 cm^{-1}) of intramolecular vibrational frequencies are IR active. As can be seen in the Fig.4, four strong peaks in FTIR transmission spectrum are observed, in good agreement with the 4 lines for pure C_{60}. Besides, the additional 5 lines appeared and are in good agreement with the work of Rao[18] on phototransformed C_{60} film, which is due to photoinduced polymerization of C_{60} films. It is indicated that the icosahedral symmetry of the C_{60} molecule has indeed been lowered. Based on the similarity of their spectra and Fig.4, we proposed that the C_{60} polymer could also be formed under the low energy Na^+ ion bombardment.

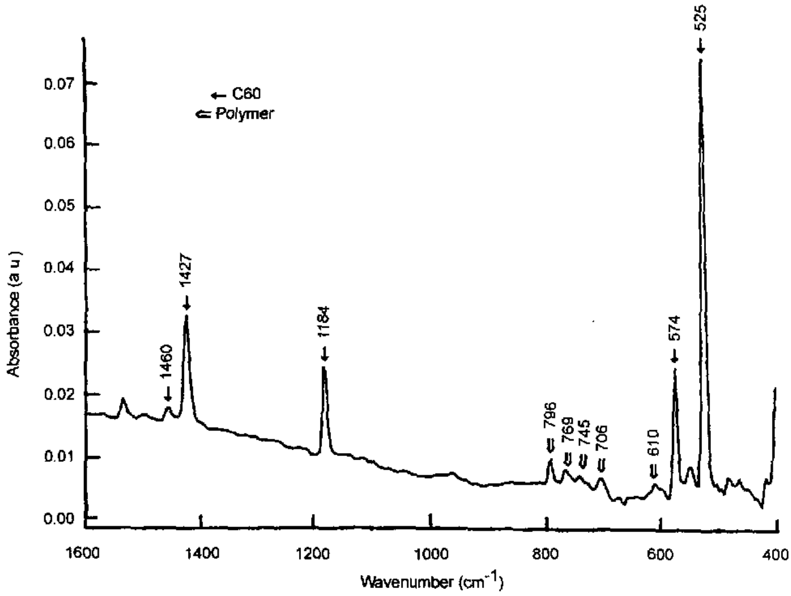

Fig.4 FTIR spectrum of a deposition film produced from a C_{60} vapour impacted with Na^+ ion

2+2 cycloaddition is a well known photochemical or thermal mechanism leading to the covalent attachment of adjacent molecules. Photochemical 2+2 cycloaddition of two molecules A and B has been found to be generally active in a variety of cases. The mechanism involves the reconfiguration of double bonds on A and B: if carbon double bonds (C=C), one on A and the other on B, are oriented parallel to one another, and separated by less than ~0.42 nm, then by photochemical assistance both these double bonds are broken and reform as four-sided ring. In our case, the additional Na^+ ions are used into preparing one C_{60} molecule through energy transfer in the lowest excited triplet state, which must have a sufficiently long lifetime, and this excited C_{60} molecule reacts with the adjacent molecule(C_n, n=56,58,62,64 etc.) which remains in the former singlet state. These requirements could be met in the collision of C_{60} vapour with energetic Na^+ ion beam. The adjacent C_{60} molecules can adopt favourable orientations, which would promote the 2+2 cycloaddition reaction.

4 CONCLUSION

The reaction of neutral C_{60} vapour impacted with energetic Na^+ ion beam was investigated. For the systems presented in this paper, endohedral fullerene $Na@C_{60}^+$ was observed obviously. Charge transfer reaction appeared to be quite efficient in positively charged spectrum. Probably because C_{60} is an electron rich system with low ionization energy (~7.61 eV), when collision with positive Na^+ ion, one would expect efficient electron capture by the atomic ions.

Substitutional products were observed in negatively-charged spectrum for collision-induced reaction of Na^+ with C_{60}, yielding a series of $C_{59-2n}Na^-$ (n=0,1,2 ···) products by C_2 loss. Consequently, the $C_{59-2n}Na^-$ always loses the Na atom during decomposition, suggesting that Na center is rather unstable. Therefore, a series of odd numbered cluster appeared in negatively-charged TOF spectra. FTIR studies of deposited C_{60} film yielded similar results to those found for photochemical transformation of C_{60} films. It seems that Na^+ ion-induced collision with C_{60} leads to the polymerization of C_{60}^+ molecule with 2+2 cycloaddition reaction.

For confirmation of the endohedral $Na@C_{60}^+$, further EXAFS study is needed.

Acknowledgement

One of us (S. - H. Lin) acknowledges the help from the experimental group in Max Born Institute, Germany, especially the discussions with Prof. E.E.B. Campbell. We are indebted to Prof. Zheng Lan-Sun *et al.* in the Chemistry Department of Xiamen University for TOFMS measurements.

References

1 Hawkins J M, Meyer A, Lewis T A *et al.* Science, 1991, **252**:312
2 Murry R L, Scuseria G E. Science, 1994, **263**:791
3 Weiske T, Bohme D K, Hrusak J *et al.* Angew Chem Inst Ed Engl, 1992, **30**:884
4 Ross M M, Callahan J H. J Phys Chem, 1991, **95**:5720
5 Weiske T, Hrusak J, Bohme D K *et al.* Helv Chim Acta, 1992, **75**:79
6 Mowrey R C, Ross M M, Callahan J H. J Phys Chem, 1992, **96**:4755
7 Campbell E E B, Ehlich E, Heilscher A *et al.* Z Phys, 1992, **D23**:1
8 Kleiser R, Sprang H, Furrer S *et al.* Z Phys, 1993, **D28**:89
9 Wan Z, Christian J F, Anderson S L. J Chem Phys, 1993, **99**:3468
10 Christian J F, Wan Z, Anderson S L. Phys Rev Lett, 1992, **69**:1352
11 Wan Z, Christian J F, Basir Y *et al.* J Chem Phys, 1993, **99**:5858
12 Christian J F, Wan Z, Anderson S L. J Phys Chem, 1992, **96**:3574
13 Christian J F, Wan Z, Anderson S L. Chem Phys Lett, 1992, **199**:373
14 Christian J F, Wan Z, Anderson S L. J Phys Chem, 1992, **96**: 10597
15 Tellgmann R, Krawez N , Lin S H *et al.* Nature, 1996, **382**:407
16 Ohno K, Maruyama Y, Esfarjani K *et al.* Phys Rev Lett, 1996, **76**:3590
17 Cui Y L, Lin S H, Rong T W *et al.* Chem Phys Lett, 1994, **227**:567
18 Rao A M, Zhao P, Wang K A *et al.* Science, 1993, **259**:955