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DOCUMENTATION PAGE

1a. REPOI Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE DTIC ELECTE JUN 04 1992 A D		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Report 38		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of Florida	6b. OFFICE SYMBOL (if applicable)	7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217-5000	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Florida Gainesville, FL 32611-2046	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-J-1248		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217-5000	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO. WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Ionization Potentials and Electron Affinities of Semiconductor Clusters Determined Via Charge Transfer Reactions			
12. PERSONAL AUTHOR(S) S.B.H. Bach, J.E. Bruce, R. Ramanathan, C.H. Watson, J.A. Zimmerman, and J.R. Evler			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 1/89 TO 2/92	14. DATE OF REPORT (Year, Month, Day) May 28, 1992	15. PAGE COUNT 15
16. SUPPLEMENTARY NOTATION To appear in "On Clusters and Clustering: From Atoms to Fractals", P.J. Reynolds, ed., Random Materials and Processes Series, North Holland, Amsterdam, 1993.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Ionization Potentials, Electron Affinities, Semiconductor Clusters, Cluster Ion Reactions	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>This chapter summarizes ONR-supported work in Prof. Eyler's laboratories involving small clusters of As, C, and P. Charge transfer bracketing experiments involving cluster ions and neutral molecules of known electron affinities (E.A.) and ionization potential (I.P.) lead to precise estimates of E.A.'s and I.P.'s for the clusters studied.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. John C. Pazik		22b. TELEPHONE (Include Area Code) 202-696-4410	22c. OFFICE SYMBOL

92 6 03 052

OFFICE OF NAVAL RESEARCH

Grant N00014-87-J-1248

R & T Code 4134052

TECHNICAL REPORT NO. 38

Ionization Potentials and Electron Affinities
of Semiconductor Clusters Determined via
Charge Transfer Reactions

by

S.B.H. Bach, J.E. Bruce, R. Ramanathan,
C.H. Watson, J.A. Zimmerman, and J.R. Eyster

To appear in

"On Clusters and Clustering: From Atoms to Fractals",
P.J. Reynolds, ed., Random Materials and Processes Series,
North Holland, Amsterdam, 1993

University of Florida
Department of Chemistry
Gainesville, FL 32611-2046

May 28, 1992

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clusters of arsenic, As_n ($n = 1 - 5$)²², carbon, C_n ($n = 3 - 32$)²³, and phosphorus, P_n ($n = 1 - 4$)²², and electron affinities (EA's) for small and large carbon clusters ($n = 4 - 8, 60, 70$) have been determined by charge transfer bracketing reactions. This technique appears to be applicable to many non-metallic clusters with IP's $> ca. 6.5$ eV and/or EA's < 3.5 eV, and gives results with uncertainties of ca. 0.1 eV. When comparisons can be made, the IP's and EA's found by this method are almost always in good agreement with well-established experimental and theoretical values, and many IP's have also been measured in this work which have not previously been determined. Of particular interest is the observation of a periodicity in carbon cluster IP's, with clusters containing $4n + 3$ atoms ($n = 1 - 6$) possessing a lower I.P. than neighboring clusters in the series.

2. Experimental

The experimental methodology employed in these studies has been discussed in some detail²³, and so will only be outlined briefly here, with attention paid to recent modifications of the approach not reported in the earlier literature.

Ions are formed by direct laser desorption from GaAs (arsenic clusters), graphite (carbon clusters), and InP (phosphorus clusters) using the focussed output of a pulsed CO_2 laser. The laser beam is introduced into the FTICR chamber through a ZnSe window, focussed by a 3 in focal length ZnSe lens through two holes on opposing trapping plates of the FTICR cell, and onto the sample of interest (see Fig. 1). The resultant plume of laser-desorbed ions, neutrals, and electrons enters the FTICR cell, where either positive or negative ions are trapped by the combined action of magnetic and static electric fields.

Carbon cluster ions C_n^+ with $n = 6 - 24$ are produced reproducibly by CO_2 laser irradiation of graphite²³. However, to form smaller ($n = 3 - 5$) and larger ($n = 25 - 32$) positive cluster ions, the doubled output of a Nd:YAG laser is focussed onto the graphite sample using an internal 3 in. (for $n = 3 - 5$ clusters) or a 1 m focal length quartz lens mounted just outside a quartz window on the FTICR vacuum chamber. Negative carbon cluster ions ($n = 4 - 8$) are formed from graphite using either the CO_2 laser as described above or the 532 nm output of the Nd:YAG laser, focussed using a 3 in focal length quartz lens. C_{60}^- and C_{70}^- are formed by CO_2 laser desorption from an extract of carbon "soot"²⁴ containing appreciable quantities of C_{60} and C_{70} .

All cluster ions but one are next ejected from the FTICR cell by exciting them to sufficiently high translational energies that they strike the plates of the cell¹⁷ and are neutralized. A pulsed valve is then used to introduce a "thermalizing" gas (Ar or SF_6) into the cell, in order to provide a number (> 100) of collisions to relax translational and internal energy of the trapped cluster ions. For work with arsenic, phosphorus, and both smaller and larger carbon cluster ions, the thermalizing gas pressure is allowed to rise into the low to mid 10^{-5} torr range, and is then pumped away rapidly in the next 1 s or

so²⁵. Some small As and P cluster ions react with SF₆, so Ar is used as a thermalizing gas for studies of their charge transfer reactions, even though it is not expected to relax excess internal energy as well as SF₆.

Any ions which might form from ion/molecule reactions of the cluster ion of interest during the thermalizing time are next ejected from the FTICR cell, leaving only near-thermal cluster ions of a single charge-to-mass ratio remaining in the cell. The ejection of unwanted ions is carried out carefully to avoid excess kinetic energy being imparted to the ion of interest when ions of nearby charge-to-mass ratio are ejected.

The charge transfer reaction of the cluster ion of interest with a neutral molecule of known ionization potential or electron affinity (Table I), which is present at low (1 - 3 x 10⁻⁸ torr) pressures in the FTICR cell is next monitored for a period of time ranging from 1 to 10 s. The intensity of both the reacting cluster ion and any product ions formed by ion/molecule reactions can be followed as a function of reaction time. In many cases reactions other than charge transfer are observed. In other (desirable) cases, charge transfer to form the parent ion of the neutral molecule of known ionization potential or electron affinity, or no reaction at all, are observed. The ionization potential (electron affinity) of the cluster species of interest is bracketed between the IP (EA) of those compounds with which the cluster ion reacts by simple charge transfer, and those with which it does not react.

The various neutral molecules of known ionization potential and electron affinity are obtained from commercial sources and used without further purification except for repetitive freeze-pump-thaw cycles. Excitation, detection, and subsequent Fourier transformation of ion signals is done using conditions previously reported²³.

3. Results

3.1 Ionization Potentials. The IP's found²² for small phosphorus and arsenic clusters are given in Table II. The cluster IP is reported as the value halfway between the IP of the compound of lowest IP for which charge transfer (CT) was not observed and the IP of the compound of highest IP for which it was observed. For example, As₃⁺ did not undergo charge transfer with m-toluidine, but did react via CT with azulene (cf. Table I). Since the IP of the cluster can lie anywhere in the gap between the two neutral IP's, the uncertainty stated is generally $\pm 1/2$ the gap size, or ± 0.1 eV when 1/2 of the gap is smaller than this amount.

The carbon cluster ionization potentials determined in these laboratories^{23,27} are given in Table III, again bracketed via CT reactions with the compounds in Table I. An interesting alternation in IP is seen for the carbon clusters, with every fourth cluster having a lower IP than those above or below it. These values have been underlined in the table.

3.2 Electron affinities. Reactions of negative carbon cluster ions have been followed in a manner exactly analogous to the positive ion studies outlined above. Electron affinity values determined for C_4 - C_8 and C_{60} and C_{70} are given in Table IV. Those for the larger clusters (fullerenes) are in quite good agreement with earlier photoelectron results³¹, but those for the smaller clusters are substantially below values reported previously².

4. Discussion

With any method that purports to determine physical properties it is important to assess the accuracy of the values obtained, particularly when many of them have not been reported previously. Comparison with well-established numbers from earlier work is useful in determining if newly acquired quantities are reliable. Such validation is discussed below for both the ionization potential and electron affinity determinations carried out in these laboratories.

4.1 Ionization potentials. Values for the As and P ionization potentials have been determined previously by spectroscopic methods, and are thus known to high precision (and, hopefully, accuracy). Carbon cluster IP's have not been measured with any precision prior to this work, as can be seen from Table III. The four previously-reported IP values (for As, P, P_2 , and P_4) judged most reliable by the authors of Ref. 26 are contained within the error limits (two cases) or are no more than 0.1 eV below the lower limits for the IP's determined by the charge transfer bracketing method. This suggests that most translational or internal energy has been removed from the cluster ions after the "thermalization" period, with a total residual energy of no more than 0.1 eV remaining. The IP's of "hot" ions would appear to be higher than their true values since their excess energy would facilitate charge transfer to a neutral of slightly higher IP than would be the case for completely thermalized ions. Incomplete thermalization is perhaps not surprising for P_4 , for which the 100 - 300 collisions it can be estimated to make with SF_6 during the thermalization period might not be sufficient to remove all of its internal energy. However, this number of collisions has been shown³² to thermalize the kinetic energies of ions formed by electron impact in an icr cell, so we would expect better agreement between charge transfer bracketing and spectroscopic results for the As ionization potential. The 0.1 - 0.3 eV discrepancy for As cannot be explained at this time.

Ionization potentials for As_2 through As_5 and for P_3 should be more reliable than earlier determinations (where they exist) which, in general were obtained by electron impact appearance potentials. Thresholds for the appearance of fragment ions following electron ionization have generally been found to decrease as improved instrumentation, or the application of photoionization techniques, is used for their determination. Thus our bracketing measurements should provide more reliable IP's, particularly for As_2 and As_4 , where we find values lower than those previously reported.

Accurate experimental IP's for small clusters can be quite useful for testing the quality of new theoretical calculations of cluster properties. The P_4 IP's (and the existence of 2 different P_4^+ isomers) reported in Ref. 22 have already stimulated at least one new theoretical calculation.³³

The carbon cluster IP's show an interesting alternation, with clusters having $4n+3$ atoms ($n = 1-6$) exhibiting IP's markedly lower than those of neighboring clusters³⁴. It is interesting to note that these are precisely the cluster sizes which have been identified as "magic numbers", possessing special stability³⁵. Since the relative abundances of neutral clusters are most often identified by ion detection after multiphoton ionization, our work suggests that clusters of these sizes **may not possess any special stability**, but rather that they are simply more easy to ionize because of their lower IP's³⁶. Because the IP of an atom or molecule is given by the difference between the energies of the neutral molecule and corresponding positive ion, it is difficult to attribute trends in IP's exclusively to trends in either neutral or ion structures. However, carbon clusters with $4n+3$ atoms might give rise to cations with $4n+2$ π electrons, which would exhibit enhanced stability if they possessed a conjugated π electron system (thus leading to a lower IP for the neutral cluster). If this were the case, and the neutrals also had a conjugated π electron system, then carbon clusters with $4n + 2$ atoms (and also this number of π electrons) should be more stable and exhibit higher IP's. Such a trend can also be seen in Table III, although not as strikingly as the lowered IP's, which are underlined.

Superimposed on the alternation of IP's discussed above is a general decrease in ionization potential with increasing n . However, even for $n = 31$ the cluster IP (7.9 ± 0.3 eV) remains considerably above the value for bulk graphite of $3.9 - 4.44$ eV,³⁷⁻³⁸ depending on its form. Even for clusters in the $C_{50} - C_{200}$ range, IP's have been found²⁷ to remain in the $6 - 7$ eV range, still much higher than the bulk. This may be due in part to the fullerenic structures of these clusters, which are not similar to the layered structure of bulk graphite.

4.2 Electron Affinities. The EA's determined for C_{60} and C_{70} are in quite good agreement with those found by laser photodetachment of negatively charged carbon clusters.³¹ Since the photodetachment experiments should determine vertical electron affinities, while charge transfer bracketing gives rise to adiabatic EA's and IP's,²² one might expect somewhat lower values from charge transfer bracketing. This is, in fact, definitely the case for $C_4 - C_8$, where values from these laboratories are about 2 eV lower than EA's reported earlier.² A discrepancy this large between vertical and adiabatic EA's is quite unexpected. Experiments are underway to investigate causes for these large differences, including some remaining unrelaxed internal energy in the negative cluster ions, or differing structures for ions formed by direct laser desorption vs. in supersonic expansions².

4.3 Limitations of the Technique. Although IP's and EA's of some species can be determined in a straightforward manner by charge transfer bracketing in the

FTICR mass spectrometer, it is worthwhile noting some limitations of the technique, a few of which have already been mentioned above. 1) If reactions other than charge transfer take place between the cluster ion of interest and the neutral molecule, bracketing is either somewhat complicated or not possible at all. Such reactivity has been seen for a reasonable number of ions and neutral species, particularly the smaller As and P cluster ions. Of course, these ion/molecule reactions may be of interest in their own right.²² 2) The precision of any bracketing approach will depend on how closely spaced are the known IP's or EA's of neutral charge transfer agents. Given the possibility of reactions other than charge transfer, a gap of several tenths of an eV might exist between the IP's or EA's of the two species which react only by charge transfer with the cluster ion, and thus can be used to bracket its IP or EA. 3) It will be difficult to extend the approach to determination of IP's < ca. 7 eV and/or EA's > ca. 3 eV, due to the lack of suitable reference compounds. Some promising di-nitrogen compounds³⁹ may lower the accessible IP range closer to 6 eV. 4) While large carbon clusters can be produced by direct laser desorption in the FTICR cell, it is difficult to make clusters of many other species which are composed of a large number of atoms. Supersonic expansion sources are more appropriate for the formation of the larger clusters. Thus the cluster sizes whose EA's and IP's can be determined by bracketing are limited, at least given the present instrumentation in these laboratories. 5) Finally, the question remains as to how close to thermal the ion energies have approached before reacting, with some indication (as discussed above) that 0.1 eV (or more in the case of small negative carbon clusters) translational and/or internal energy remains.

5. Conclusions

The IP's of arsenic, carbon, and phosphorus clusters have been determined by charge transfer bracketing in an FTICR mass spectrometer to a precision of a few tenths of an eV. The results are in reasonable agreement with previous reliable experimental IP determinations, and provide the first values necessary to follow the trend of IP's from single atoms to the bulk. They also have served as standards against which to test new theoretical IP calculations. The techniques should be useful for studying numerous other small clusters with IP's > ca. 6 eV or E.A.'s < ca. 3.0 eV, whose ions can be produced by direct laser vaporization. Results for carbon clusters indicate that the unusual stability of certain cluster sizes may result solely because of the lower ionization potentials of these clusters.

Acknowledgment

This work was supported by the Office of Naval Research.

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Table I
Charge Transfer Compounds Used in Bracketing Experiments

<u>IP²⁶</u> <u>(eV)</u>	<u>Compound</u>
6.83	N,N-diethyl-p-toluidine
6.93	N,N-dimethyl-p-toluidine
7.00	N,N-diethylaniline
7.13	N,N-dimethylaniline
7.41	azulene
7.50	m-toluidine
7.72	aniline
7.78	phenyl-1,4-benzoquinone
7.80	2-naphthol
7.85	hexamethylbenzene
8.04	durene
8.13	p-cresol
8.29	m-cresol
8.44	p-xylene
8.56	m-xylene
8.69	p-chlorotoluene
8.82	toluene
8.89	p-dichlorobenzene
9.04	1,2,4-trichlorobenzene
9.11	m-dichlorobenzene
9.18	1,4-difluorobenzene
9.20	fluorobenzene
9.25	benzene
9.30	1,2-difluorobenzene
9.32	tetrachloroethylene
9.35	1,3-difluorobenzene
9.45	2-nitrotoluene
9.48	3-nitrotoluene
9.56	1,4-naphthoquinone
9.88	1-fluoro-3-nitrobenzene
9.91	hexafluorobenzene
10.04	1,4-benzoquinone
10.10	1,2-dicyanobenzene
10.10	1,4-dicyanobenzene
10.23	4-nitrobenzotrile
10.29	3-nitrobenzotrile
10.30	1,4-dinitrobenzene
10.43	1,3-dinitrobenzene

10.507	ethylene
10.528	ethylene-d ₄
10.57	hexafluoro-m-xylene
10.7	tetrafluoro-1,4-benzoquinone
11.18	difluoroacetylene
11.394	acetylene
11.4	phosphorous trifluoride
11.77	tetracyanoethylene
12.130	xenon
12.194	acetonitrile
12.89	nitrous oxide
13.04	sulfuryl fluoride
13.77	carbon dioxide
13.997	krypton

<u>EA²⁶</u> <u>(eV)</u>	<u>Compound</u>
0.86	3-nitro-o-xylene
0.99	3-nitrotoluene
1.10	1,4-dicyanobenzene
1.23	1-fluoro-3-nitrobenzene
1.41	3-nitro- α, α, α -trifluorotoluene
1.56	3-nitrobenzonitrile
1.61	2-nitrobenzonitrile
1.65	1,3-dinitrobenzene
1.72	4-nitrobenzonitrile
1.81	1,4-naphthoquinone
1.91	1,4-benzoquinone
2.00	1,4-dinitrobenzene
2.16	3,5-dinitrobenzonitrile
2.19	2,3-dichloro-1,4-naphthoquinone
2.44	2,5-dichloro-1,4-benzoquinone
2.48	2,6-dichloro-1,4-benzoquinone
2.70	tetrafluoro-1,4-benzoquinone
2.78	tetrachloro-1,4-benzoquinone
3.17	tetracyanoethylene

Table II
As_n and P_n Ionization Potentials Determined
by Charge Transfer Bracketing Reactions

<u>Species</u>	<u>Ionization Potential</u>	
	<u>This work</u>	<u>Literature*</u>
As	10.00 ± 0.10	9.7883
As ₂	9.89 ± 0.10	(10.1 ± 0.2)
As ₃	7.46 ± 0.10	NA
As ₄	8.63 ± 0.10	(9.07 ± 0.07)
As ₅	7.95 ± 0.10	NA
P	10.50 ± 0.10	10.486
P ₂	10.6 ± 0.1	10.53
P ₃	8.09 ± 0.10	(7.85 ± 0.2)
P ₄	9.28 ± 0.10**	9.08 ± 0.05
	9.23 ± 0.10**	

* Values in parentheses are those which are "considered not to be firmly established"²⁶ and contain a higher degree of uncertainty.

** Two isomeric forms of P₄ are present, see Ref. 22.

Table III
 C_n Ionization Potentials Determined by Charge Transfer Bracketing

<u>Species</u>	<u>IP (in eV) (this work)</u>	<u>IP (in eV) (lit)</u>	
		<u>Expt'l.</u>	<u>Theory</u>
C_3	13.3 +/- 0.4	(12.3 +/- 0.3) ^a	11.4 ^b
C_4	12.9 +/- 0.8	(12.6) ^a	10.5
C_5	12.9 +/- 0.8	9.98 - 12.84 ^c	10.7
C_6	9.6 +/- 0.3	"	9.8
C_7	<u>8.1</u> +/- 0.1	"	10.0
C_8	8.8 +/- 0.1	6.42 - 12.84 ^c	9.2
C_9	8.8 +/- 0.1	"	9.4
C_{10}	9.1 +/- 0.1	"	
C_{11}	<u>7.45</u> +/- 0.1	"	
C_{12}	8.5 +/- 0.1	"	
C_{13}	8.1 +/- 0.1	"	
C_{14}	8.5 +/- 0.1	"	
C_{15}	<u>7.2</u> +/- 0.1	"	
C_{16}	8.1 +/- 0.1	"	
C_{17}	8.1 +/- 0.1	"	
C_{18}	8.1 +/- 0.1	"	
C_{19}	<u>7.4</u> +/- 0.1	"	
C_{20}	8.2 +/- 0.2	"	
C_{21}	8.2 +/- 0.2	"	
C_{22}	8.2 +/- 0.2	"	
C_{23}	<u>7.2</u> +/- 0.3	"	
C_{24}	7.9 +/- 0.2	"	
C_{25}	8.0 +/- 0.3	"	
C_{26}	7.8 +/- 0.1	"	
C_{27}	<u>7.6</u> +/- 0.1	"	
C_{28}	7.8 +/- 0.1	"	
C_{29}	8.1 +/- 0.1	"	
C_{30}	7.9 +/- 0.2	"	
C_{31}	<u>7.9</u> +/- 0.3	"	
C_{32}	<8.04		

Table III, continued

^aGiven in Ref. 26, but stated to be less reliable than other values in the table.

^bAll theoretical values from Ref. 28.

^cRef. 29.

Table IV
C_n Electron Affinities Determined by Charge Transfer Bracketing

<u>Species</u>	<u>EA (in eV) (this work)</u>	<u>EA (in eV) (lit)</u>	
		<u>Exp'l.</u>	<u>Theory</u>
C ₄	1.3 +/- 0.1	3.70 ^a	3.41 ^b
C ₅	1.5 +/- 0.1	2.80 ^a	2.43
C ₆	1.5 +/- 0.1	4.10 ^a	3.69
C ₇	1.6 +/- 0.1	3.10 ^a	
C ₈	1.6 +/- 0.1	4.42 ^a	
C ₆₀	2.6 +/- 0.1	2.6-2.8 ^c	
C ₇₀	2.6 +/- 0.1	2.6-2.8 ^c	

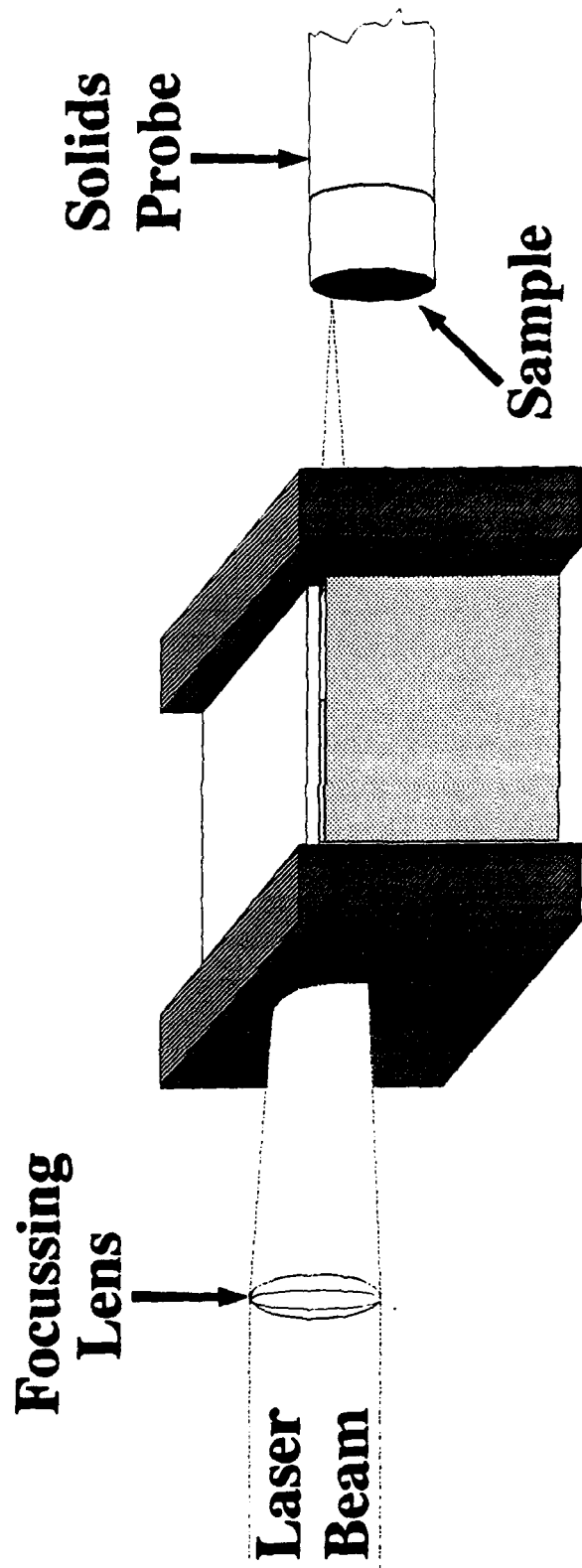
^aRef. 2.

^bAll theoretical values from Ref. 30.

^cRef. 31.

Figure Caption

Figure 1. Schematic representation of the laser focussing arrangement and FTICR analyzer cell used for cluster ion formation, reactivity studies, and detection.



FTICR Cell