QWG3 Gallium arsenide cluster reactions with NO

L. H. Wang, L. P. F. Chibante, F. K. Tittel, R. F. Curl, and R. E. Smalley
Rice Quantum Institute, Rice University, Houston, Texas 77251-1892

Semiconductor cluster ions can be observed with extremely high mass resolution (of the order of 10^5) with a Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer. Various physical and chemical processes can be implemented with a given environment for tens of seconds in the FT-ICR trap.[1,2]

Previously, the reaction pattern of $Ga_xAs_y^+$ clusters with NH_3 was observed,[1] and $Ga_xAs_y^-$ clusters exhibited no reaction toward NH_3. *Recently, the reaction of both positive and negative* Ga_xAs_y ($x+y$ = 9 to 16) clusters with NO was studied. A pronounced even/odd alternation was observed (Figs. 1 and 2), and the even-numbered singly charged clusters are more reactive than the odd-numbered ones. This indicates the odd-numbered singly charged GaAs clusters have closed-shell singlet ground states. The even-numbered ones that have an odd number of valence electrons are necessarily open shell. Nitric oxide, a free radical with an unpaired electron, apparently can sense the free radical nature of the singly charged GaAs clusters. In contrast, the closed-shell reagent, ammonia, showed no evident reaction preference for even-numbered or odd-numbered positive GaAs clusters. In earlier work, photoionization studies of the neutral GaAs cluster beam revealed a strong even/odd alternation in the ionization potentials,[2] and photodetachment studies of the negative clusters showed corresponding odd/even alternation in the electron affinities of the clusters.[3,4]

Nitric oxide was found to etch $Ga_xAs_y^-$ ($x+y=10$) clusters (Fig. 3). Two possible reaction channels appear to be

$$Ga_xAs_y^- + NO = Ga_{x-2}As_yN^- + Ga_2O,$$

$$Ga_xAs_y^- + NO = Ga_{x-5}As_y^- + Ga_5NO.$$

In this reaction, Ga-rich negative clusters are more reactive and $Ga_7As_3^-$ has the maximum reactivity among $Ga_xAs_y^-$ ($x+y=10$) clusters. The GaAs clusters produced in the supersonic cluster beams are normally Ga-rich, and the second reaction provides a means for producing As-rich clusters. As_5^- clusters are products as labeled in Fig. 3.

Because of the mass degeneracy[1] in GaAs cluster ion mass spectroscopy, a deconvolution is necessary to determine the concentrations of different stoichiometry. The numbers shown in different panels of Fig. 3 give the number of Ga atoms, the number of As atoms, and the relative concentrations, respectively. It can be clearly seen that the parent becomes more As-rich as the reaction develops.

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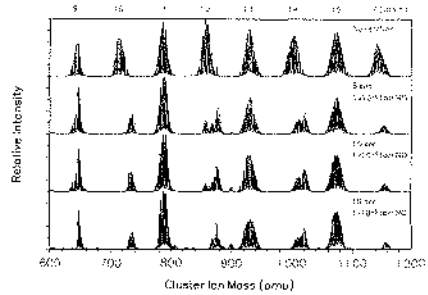
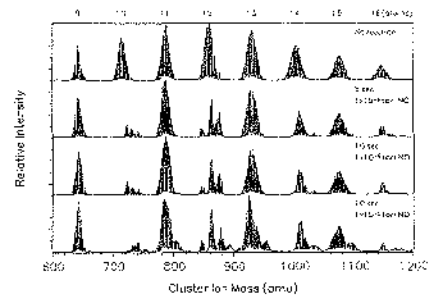
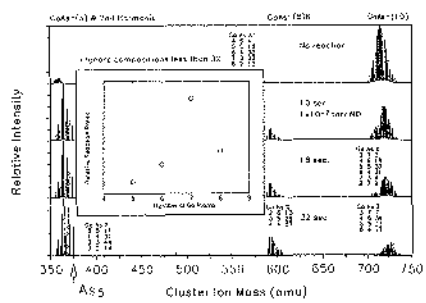
1. L. H. Wang, L. P. F. Chibante, F. K. Tittel, R. F. Curl, and R. E. Smalley, Chem. Phys. Lett. **172**, 335 (1990).
2. S. C. O'Brien, Y. Liu, Q. Zhang, J. R. Heath, F. K. Tittel, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **84**, 4074 (1986).
3. Y. Liu, Q. L. Zhang, F. K. Tittel, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **85**, 7343 (1986).
4. C. Jin, K. Taylor, J. Conceicao, and R. E. Smalley, Chem. Phys. Lett., in press.



QWG3 Fig. 1. Mass spectrum of the reaction between $Ga_xAs_y^-$ ($x+y$ = 9 to 16) and NO, which shows even/odd alternation in reactivity.



QWG3 Fig. 2. Mass spectrum of the reaction between $Ga_xAs_y^-$ ($x+y$ = 9 to 16) and NO, which depicts even/odd alternation in reactivity.



QWG3 Fig. 3. Mass spectrum of the reaction between $Ga_xAs_y^-$ ($x+y$ = 10) and NO, which shows two reaction channels. The protected area shows the relative reactivities of different compositions with respect to $Ga_4As_6^-$. The three columns of data in each panel show the number of Ga atoms, the number of As atoms, and relative concentrations; compositions <3% are ignored.