Transient chemical forms of molecular ions emitted from a graphite surface by N₂ laser excitation

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Laser-induced molecular-ion emission from a graphite crystal has been investigated with spectrometers of the time-of-flight (TOF) type and of quadrupole mass (QM) one. Both types of measurements show mass spectra entirely different from each other. The difference comes from the fact that the TOF method identifies the mass-to-charge ratio of emitted ions within a period less than 1 μs after emission, whereas the QM measures the ratio in more than 20 μs. Our TOF detects ions of the molecular form C_{3i}^{2+} ($i = 1, 2, 3, \ldots$) under positive field acceleration as well as C_{3i}^{2-} under a negative one. A separate measurement by a 127° cylindrical electrostatic energy analyzer determines the average time required for C_3^{2+} ions to disintegrate into C_1^{+} from the plot of transit time through the analyzer versus the deflecting field. This transformation time is estimated to be 9 ± 1.6 μs under the pulsed-laser-field intensity of 10 to 100 MW/cm^2 and its pulse width of 10 ns.

The interaction of solid surfaces with intense laser radiation has been a subject of considerable research for understanding the details of physical process for transferring laser energy to the lattice system via electronic excitations.[1-3] Particle emissions have been observed from the sample surface during and immediately after laser excitations.[4-6] By analyzing the chemical species and energy distributions of emitted neutral atoms, molecules, and their ions, one may obtain such information as the time variation of lattice temperature, the induced change in the chemical bond at the surface under such a high level of excitation.[4]

This Rapid Communication reports the time-of-flight (TOF) measurement of molecular ions emitted from graphite surfaces under N₂ laser irradiation. The chemical forms of emitted species are found different from those identified by a quadrupole-mass (QM) spectrometer. The difference is attributed to the emission of unstable molecular-ion species which subsequently disintegrate into more stable forms of ion. This interpretation provides a reasonable explanation for ion species observed by the QM measurement.

The light beam from a N₂ laser (photon energy 3.68 eV, the peak intensity 10 to 100 MW/cm², and pulse width 10 ns) is incident slightly off normal (5 to 10 deg) to the basal plane of graphite (highly oriented pyrolitic graphite) which is placed in a vacuum chamber. The base pressure of the vacuum system is less than 10⁻⁷ Pa. Ions emitted from the sample surface are accelerated at a right angle to the laser beam towards the entrance aperture of the TOF mass spectrometer. The spectrometer consists of a two-stage aperture lens for ion acceleration followed by a 62-cm-long drift tube. Ions are detected by an electron multiplier connected to a wave memory system which has the sampling rate of 0.1 μs per channel. Except for the initial kinetic energy measurements explained later, the fixed voltages of 30, 300, and 300 V have been applied to the electrodes of the first lens, second lens, and the drift tube, respectively. The QM analysis is also performed by replacing the TOF spectrometer by a conventional QM spectrometer capable of detecting the mass-to-charge ratio up to 300 amu with the quadrupole field length of 20 cm.

Figure 1 shows spectra measured by the TOF spectrometer for (a) positive and (b) negative ions. The voltage of the drift tube, V_d, is set at 300 V with respect to the sample potential. The relative intensities of the peaks can vary within $\pm 15\%$ from pulse to pulse of the incident laser beam. These spectra represent typical results as recorded for each laser shot. The first peak with the shortest flight time in Fig. 1(a) may be identified as due to $(C_3^{2+})_l$ ($l = 1, 2, 3, \ldots$). To assign the value of l, one may compare the difference in the formation energy of ionic clusters between l and $l + 1$. For example, the formation energy $F^s(C_3^{2+})$ for a C_3^{2+} cluster from a solid surface may be estimated from

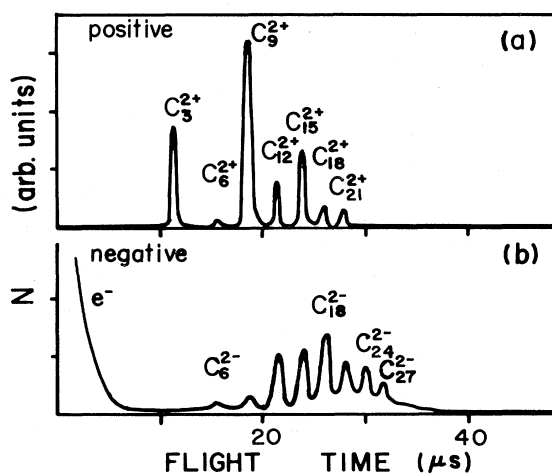$$F^s(C_3^{2+}) \cong 3D^s(C) + 2I^g(C^+) + F^g(C_3^{2+}) \; ,$$

FIG. 1. Time-of-flight spectra of molecular ions emitted from graphite under N₂ laser irradiation for (a) positive and (b) negative accelerations. The ordinate represents the number of emitted ions. The drift voltage V_d is set at 300 V. The molecular species indicated are assigned for double-charged ions.

where $D^s(C)$ is the energy required for taking out one C atom from solid surface, $I^s(C^+)$ is the ionization energy of a C atom, and $F^s(C_3^{2+})$ is the formation energy of C_3^{2+} from two C^+'s and one C. Similarly,

$$F^s(C_6^{4+}) \cong 6D^s(C) + 4I^s(C^+) + F^s(C_6^{4+}) .$$

One may estimate in approximation

$$F^s(C_6^{4+}) - F^s(C_3^{2+}) \gtrsim 20 \text{ eV} ,$$

which implies that both cluster species cannot coexist in a comparable ratio of concentration; hence $l = 1$ is the most reasonable assignment. A similar argument may be applied to assign $(C_{3i}^{2+})_i$ (i odd) with $l = 1$ for the ith peak in the spectrum of Fig. 1(a). Here one may exclude the possibility of having these ion clusters single charged in place of double, because the assignment of single charge would presume the presence of an unrealistic fractional mass number of the C atom. Likewise, one is inclined to assign the even ith peak with C_{3i}^{2+}. On the other hand, this mass number argument cannot exclude the possible contribution of $C_{(3/2)i}^+$ (i even) with its single charge and integer mass number. This charge number ambiguity can be eliminated through experimental verification on the stability of C_{3i}^{2+} (i even) as described in the latter part of this paper. The experimental results on negative ions in Fig. 1(b) may be interpreted in a similar manner. For positive ions, species with an odd i tend to be dominant over those with $i \pm 1$ [or even $3(i \pm 1)$]. The peak with $i = 3$ is most prominent. For negative ions, no such alternation in intensity takes place.

For correct interpretation of TOF measurements, one must know the initial kinetic energy of ions, eV_0, and the time spent before entering the drift tube. The total flight time t_f is expressed as $t_f = t_0 + t_{ac} + t_d$, where t_0 is the initial delay time, if any, before emission of ions from the surface after the pulsed laser excitation, t_{ac} the time required for an ion to be accelerated up to the entrance aperture of the drift tube, and t_d is the actual drift time in the drift tube. The time t_{ac} can be calculated from the distance and from the potential distribution between the sample surface and the entrance aperture of the drift tube. The calculation based on a simple estimate of the potential distribution without space charge effects shows that, for the measurement of Fig. 1, t_{ac} is less than 5% of t_d with $V_0 = 0$.

To estimate the effect of t_0 and V_0, the TOF spectrum is measured as a function of V_d. The result for the C_3^{2+} ion is shown in Fig. 2. For the approximation $t_{ac} \cong 0$, t_f for C_3^{2+} is expressed as

$$t_f = t_0 + L_d (3m/4e)^{1/2}(V_0 + V_d)^{-1/2} , \tag{1}$$

where L_d is the length of the drift tube (62 cm) and m is the mass of a carbon atom. If $V_0 = 0$ and t_0 is finite, the experimental points (solid circles) would be found on a straight line which crosses the ordinate at $t_f = t_0$ in the t_f vs $V_d^{-1/2}$ plot. On the other hand, if $t_0 = 0$ and V_0 is finite, the experimental points may yield to a straight line (crosses) which crosses at the origin in the t_f vs $(V_0 + V_d)^{-1/2}$ plot. From the results shown in Fig. 2, the best fit is obtained with $t_0 = 0$ and $V_0 = 20$ V. Hence the initial delay time t_0 can be neglected in the time scale of microseconds, and the initial kinetic energy, assuming a double charge, is estimated to be 40 eV. With this kinetic energy, the value of t_{ac} is re-
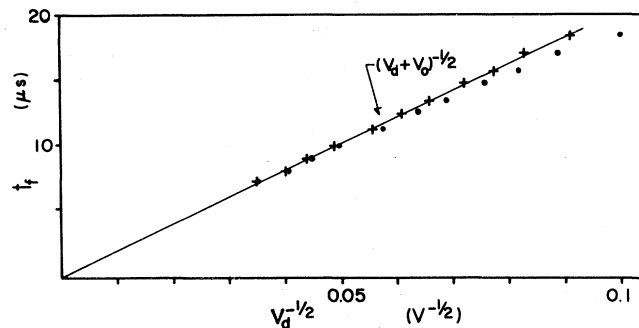

FIG. 2. The plot of the flight time t_f of C_3^{2+} ions vs inverse square root of the drift voltage V_d. Solid circles represent the measured results. Crosses are the plot of flight time vs $(V_d + V_0)^{-1/2}$ with $V_0 = 20$ V in Eq. (1), where $2eV_0$ is the initial kinetic energy of emitted ions.

duced and the total error in the mass of ion, M, in the TOF measurement in Fig. 1 is estimated to be $\Delta M/M = \pm 0.1$.

Figure 3 shows the experimental results for ion emissions from the same graphite sample measured by a QM spectrometer. Molecular ions C_n^+ ($n = 1, 2, 3, \ldots$) are observed with n up to 9. The species with an odd n is dominant over the even species of $n \pm 1$. Furthermore C_3 exhibits the maximum intensity, in contrast to C_9 in the TOF spectrum in Fig. 1. This result is similar to that reported by Berkowitz and Chapka for neutral molecules.[7] As they have pointed out, this experimental result is consistent with the stability consideration of linear carbon chains C_n's in its gas phase.[8]

It is clear from the comparison of Figs. 1 and 3 that TOF and QM experiments measure different ion species and this difference must be attributed to the difference in the process of determining the mass-to-charge ratio k. For TOF analysis, the spectrometer measures k only during the period of acceleration (t_{ac}), which is less than 1 μs under our experimental condition. Since no electric field is applied in the drift tube, flight time t_d is unaffected, in principle, by any change in k. For QM analysis, the spectrometer measures k during the entire period of the ion in the quadrupole field. This period is found longer than 20 μs for our measurements. Hence the time required to determine k by both
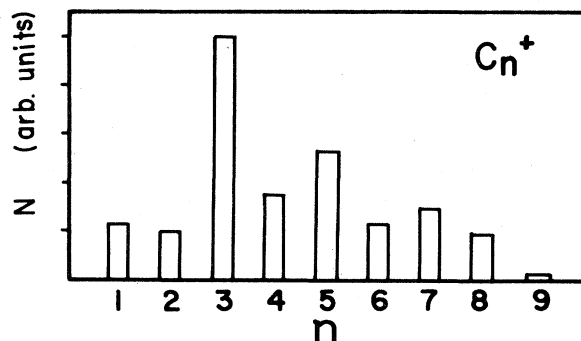

FIG. 3. Quadrupole mass spectrum of molecular ions emitted from graphite under N_2 laser irradiation for positive ions.

kinds of measurements differs from each other by about two orders of magnitudes.

The experimental results and the discussions given above lead to the conclusion that, at the time of laser excitation, unstable molecular clusters are emitted and in the time scale of submicroseconds the clusters are of the form $C_{3i}^{2\pm}$'s which disintegrate into $C_n^{\pm}$'s in times less than 20 μs. The above interpretation of the experimental result provides a reasonable explanation for the QM spectrum shown in Fig. 3: Since the QM spectrometer detects only stable ions (of lifetime longer than 20 μs), their mass-to-charge ratios are measured in a state of transition to an equilibrium with their gas phase. It is also noted that, at the time of laser excitation, emitted ion clusters are distributed possibly over their excited electronic, vibronic, and rotational states. Subsequent relaxations may result in disintegrations of clusters into simpler and more stable molecular forms.

To investigate the disintegration process during the flight time of molecular ions, the following experiment is conducted. The ions emitted from the sample after laser excitation are passed through a 127° cylindrical electrostatic energy analyzer with its mean radius $R = 3.5$ cm. The flight time t_a required for the ions to run from the sample to the exit slit of the analyzer is measured as a function of the analyzer voltage V_a applied between the two electrodes. For a given V_a the energy analyzer allows those ions having a particular value of kinetic energy divided by charge to reach the exit slit. Hence any change in k (mass-to-charge ratio) of ions during their flight time in the analyzer induces a change in t_a. Figure 4 shows the measured results. The data points are found on a straight line in the plot of t_a vs $V_a^{-1/2}$. The straight line intersects the ordinate at $t_a = 1.6$ μs. This experimental result may be interpreted as follows. Suppose that an ion of $k = k_1$ leaves the sample surface at $t = 0$ with its velocity v_1. It goes into the entrance slit of the analyzer and travels in a circular orbit under a radial electric field E_a for the distance D_1 for $0 \leq t_a \leq t_c$. The ion then dissociates into another species with $k = k_2$ and continues to travel through the circular orbit with its velocity v_2 for the distance D_2 to reach the exit slit. In order for the two forms of ions to travel in a circular orbit without any change in their orbi-

tal radius before and after disintegration, the relation $k_1 v_1^2 = k_2 v_2^2 = E_a R$ must be satisfied. The analyzer voltage V_a is related to E_a by $V_a = E_a R \ln(R_2/R_1)$, where R_1 and R_2 are radii of the inner and outer electrodes of the analyzer, respectively. For our spectrometer, $\ln(R_2/R_1) = \frac{1}{2}$. The total time t_a required for ions to travel the distance $D = D_1 + D_2$ (= 95 cm) from the sample to the exit slit of the analyzer is $t_a = D_1/v_1 + D_2/v_2$. From the above relations together with $t_c = D_1/v_1$, t_a is expressed as

$$t_a = [1 - (k_2/k_1)^{1/2}]t_c + D(k_2/2V_a)^{1/2} . \qquad (2)$$

Figure 4 shows the plot of t_a vs $V_a^{-1/2}$, where the slope of the experimental points gives the value of k_2 (after disintegration). Slopes calculated for C_3^{2+} and C_1^+ are indicated in Fig. 4 by dashed and dash-dotted lines, respectively. The slope of the experimental points shows that the ion species after disintegration is C_1^+ rather than C_3^{2+}. Hence one finds from Eq. (2) that C_3^{2+} disintegrates into C_1^+ with $t_c = 9 \pm 1.6$ μs. The time t_c may be interpreted as the characteristic time for transformation of C_3^{2+} ions into C_1^+ by fragmentation. Similar analyses applied to other ionic clusters show that the value of t_c for any molecular ion cluster is of the order of 1 μs. Hence the ionic cluster species found in our TOF spectrum exhibit a similar period of stability before their fragmentation. This result may provide additional information regarding the charge assignment on our TOF spectrum in Fig. 1. In our interpretation of the TOF spectrum an ambiguity remains in excluding the observation of singly charged ions. If singly charged ions were the dominant species, they would be observed with t_c's quite large compared to our time scale of ~ 20 μs. In this case Eq. (2) may be rewritten as $t_a = D(k_1/2V_a)^{1/2}$ on account of their considerable stability (note $k_1 = k_2$). Hence the observation of finite values of t_c implies that singly charged ions cannot be appreciable components in the spectrum.

Unstable molecular-ion emission has been observed in the spectra obtained by other ion desorption techniques such as secondary-ion mass spectroscopy (SIMS),[9] fast atom bombardment (FAB), and fission-desorption mass spectroscopy.[10] Although these various desorption measurements yield similar spectra, we notice many distinctive features in the present case of laser desorption in comparison with the atom- or ion-induced ion desorption mentioned above. Our preliminary measurement through a QM spectrometer for SIMS on the graphite sample bombarded by 1-keV nitrogen ions shows that C_1^+ is the dominant ion species in the spectrum and the intensity of C_3^+ is an order of magnitude smaller than that of C_1^+. This result is in remarkable contrast to our QM result by laser excitation as shown in Fig. 3. Other characteristic differences noted in our investigation on Si, GaAs, and GaSe (Refs. 11 and 12) are as follows: (1) Ion emission yield for any of the materials is strongly dependent on laser intensity near its threshold. In most cases molecular ions are dominant near the threshold, while atomic ions are dominant at higher intensities. (2) Average kinetic energy of the emitted ion is also strongly dependent on laser intensity. For excitation over 1 GW/cm^2 the kinetic energy can go as high as 1 keV. This experimental condition of high excitation does not apply to the present investigation. Such a high level of average kinetic energy cannot be reached in most cases of SIMS and FAB.
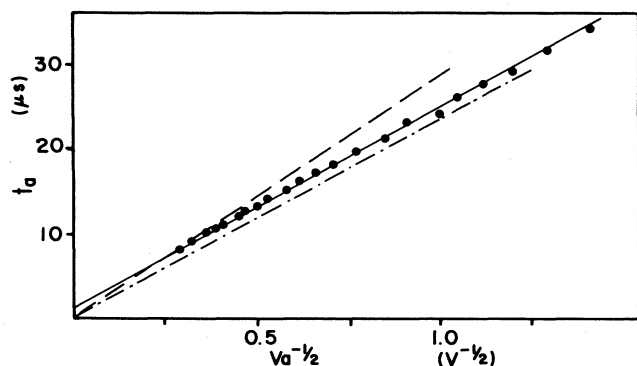

FIG. 4. The plot of flight time t_a of C_3^{2+} ions vs inverse square root of the voltage V_a applied to the energy analyzer. The extrapolation of the data points (solid circles) intersects the ordinate at $t_a = 1.6 \pm 0.2$ μs. The dashed and dash-dotted lines are drawn to indicate the slopes calculated for C_3^{2+} and C_1^+, respectively, with $t_c = 0$ in Eq. (2).

ACKNOWLEDGMENTS

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