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Refinement of the autoneutralization lifetimes of short lived states of SF_6^-

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Previous measurements of the autoneutralization lifetime of SF_6^- indicated there are multiple states (lifetimes) and that the distribution of states is controlled, at least in part, by the temperature of the SF_6 molecules prior to electron capture. These measurements indicated the existence of a short lived state with a lifetime of the order of $2\ \mu\text{s}$. The experimental apparatus has been revised to confirm the existence of the short lived state and provide a more accurate measurement of the lifetime.

INTRODUCTION

Previous measurements in our laboratory¹ have shown that for the unimolecular reaction



the rate constant k is not defined by a single state but is rather a composite of several states, each having a unique rate constant. It has been shown¹ that the SF_6^- autoneutralization process can be described by

$$N(t) = I_1[1 - e^{-(k_1 t)}] + I_2[1 - e^{-(k_2 t)}] \\ + \cdots + I_n[1 - e^{-(k_n t)}], \quad (2)$$

where $N(t)$ is the number of neutral molecules resulting from the autoneutralization of ions (I_n) in n states. The upper bound on k_n has not been determined, although results of Odom, Smith, and Futrell² indicate autoneutralizing states with lifetimes ($1/k_n$) of the order of 10 ms or more. It has been demonstrated¹ that the distribution of states is controlled, at least in part, by the temperature of the SF_6 gas prior to electron capture and, for ion source temperatures of 400–500 K, states with lifetimes of the order of μs are heavily populated. Our previous measurements¹ indicated the presence of a short lived state of $\sim 2\ \mu\text{s}$ and several (two or more) states with lifetimes of 12–17 and 22–27 μs . However the instrumental apparatus was not optimized to measure the $2\ \mu\text{s}$ component and the uncertainty was significant. To alleviate this the experimental apparatus has been modified to provide detailed data on the short lived state and the lifetimes have been measured for a variety of observation windows (time spans) at two different ion source temperatures. This has provided a more precise determination of the lifetime of the short lived state. Fast (3–25 keV) SF_6 neutrals have been shown³ to be highly efficient probes for secondary ion mass spectrometry of nonconductive materials. Since production of the fast SF_6 neutral beam relies on autoneutralization of the SF_6^- anion, optimal design and operation of ion sources for this application requires a rational understanding of the autoneutralization process, particularly for the short lived states. More accurate measurements of these processes may also help to further our understanding of molecular dynamics.

EXPERIMENTAL

The basic experimental apparatus and procedure have been described in detail in Ref. 1. A highly focused beam of

SF_6^- ions, produced by electron capture in the ion source,⁴ is directed down a flight tube that contains a series of electrostatic deflection electrodes and is terminated with a multi-channel plate array detector (MPAD) coupled to a photometer. During flight the autoneutralization of SF_6^- ions progressively increases the beam's neutral component and the ion and neutral components of the beam are separated using the deflection electrodes. By switching from one deflection electrode to the next the neutral intensity as a function of time (position) can be measured with the MPAD and photometer.

The design of the previous system resulted in ion lens residence times varying by several μs as a function of the ion acceleration voltage, restricted the first deflection electrode to a position corresponding to $\sim 4\ \mu\text{s}$ from the point of ion formation and limited the spacing of the flight tube deflection points to $\sim 2\ \mu\text{s}$. Thus this provided a very limited set of data for the short lived component. A new ion lens was designed using the SIMION⁵ program that focused the ions into a near-parallel small diameter ($\sim 1\ \text{mm}$ at 2.8 m from the source) cylindrical beam and which had a near-constant lens residence time of $\sim 2\ \mu\text{s}$ over a wide (4 to 18 kV) range of acceleration voltages. The remaining uncertainty in the calculation of the ion lens residence time is the uncertainty as to where the ions are actually produced in the source. The near-constant lens residence time made it possible to vary the maximum experimental observation time window length without significantly shifting the starting point (time). A new flight tube was constructed containing 32 deflection electrodes to provide a high density of data points for short (2 to 10 μs) flight times. The first deflection electrode was located 2.9 cm from the ion source exit aperture. This corresponds to $\sim 2\ \mu\text{s}$ from the ion formation region of the ion source. The next five electrodes were spaced at 2.5 cm intervals, the next 20 at 4.6 cm intervals and the last six at intervals of tens of cm. The last deflection electrode was 207 cm from the ion source exit aperture. This configuration permitted the experimental observation window length to be varied from 15 μs (at 18 kV acceleration) to 32 μs (at 4 kV acceleration), without significantly ($\pm 0.3\ \mu\text{s}$) changing the time position of the first deflection point and provided data points at $\sim 0.3\ \mu\text{s}$ intervals. Consideration was given to the possibility that the higher electric field gradients within the acceleration lens at 18 kV were stripping the electron from the anion and an attempt was made to determine if this was possible. The results showed that for gradients less than ~ 6

kV/cm there was no indication that electron stripping was occurring, while at higher gradients this may have been occurring (it could not be definitively proven or disproven with this apparatus). Thus the system was always operated within the range of 6 kV/cm or less. A new MPAD was installed to ensure maximum sensitivity and its linearity was carefully measured. The operating parameters (gas pressure and filament materials and temperatures) and the method of data collection and reduction were the same as described in Ref. 1.

RESULTS AND DISCUSSION

As previously demonstrated¹ the autoneutralization of SF_6^- produced via electron capture in an ion source operating in the temperature range of 375 to 555 K can be described by Eq. (2) where $n = 3$. The reader is cautioned, however, to note that although the temperature of the bulk of the source is at the stated temperature (375–560 K), the filaments are operating at ~ 1600 to 2200 K, resulting in large temperature gradients within the source. Thus the ion formation process is not in thermodynamic equilibrium and the internal energy of the molecular ion cannot be described by a temperature. The reported source temperature should only be viewed as an empirical indicator. Our previous analysis had indicated that the three lifetimes ($1/k_n$) that described the experimental data fell into the ranges of 1–2, 12–17, and 22–27 μs . It was also demonstrated that there was not a consistent set of lifetimes for $n = 2$ that predicted the measured response over the temperature range studied. Thus it was concluded that there must be at least three unique states or a quasicontinuum of states. Since it is not possible to differentiate between these two possibilities by measuring only the autoneutralization rate (a precise knowledge of the molecular energy levels of the SF_6^- anion and neutral would prob-

ably provide the necessary additional data needed to do this) we have analyzed the data assuming both possibilities.

It is generally accepted^{2,6} that the measured lifetime of SF_6^- is dependent upon the experimental observation window, a strong indication that it can not be described by a single first order exponential rate equation. This is demonstrated in Fig. 1 in which the lifetime, calculated assuming a single first order exponential of the form of Eq. (2) with $n = 1$ (this will be referred to as the composite lifetime), is shown as a function of the experimental observation time window. The measurement window width is the flight time from the first deflection electrode to the last deflection electrode. Since the lens used in these measurements had a near-constant residence time of $2.0 \pm 0.3 \mu\text{s}$ (as calculated with the SIMION lens analysis program⁵) the beginning of each time window is essentially the same, i.e., $\sim 2 \mu\text{s}$ from the ion formation point. The data for both source temperatures exhibits a clear trend with the lifetime increasing as the measurement window is lengthened. This is a result of the increased influence of the longer lived states in the curve fitting algorithm. Figure 2 shows a typical data set for the high temperature source along with the calculated single exponential fit to the data and the residuals of the fit. Note that the residuals clearly show that the single exponential is underpredicting the data at early times, slightly overpredicting for the middle period (which corresponds to the composite lifetime, 8 μs , calculated with a single exponential) and underpredicting at longer times. The quantitative differences between the composite lifetimes for the two different source temperatures also indicate that there must be more than one state, otherwise only the intensity [I_n in Eq. (2)] would change with source temperature since the observation window is independent of the source temperature. Thus some combination of exponentials is necessary to successfully model the experimental results.

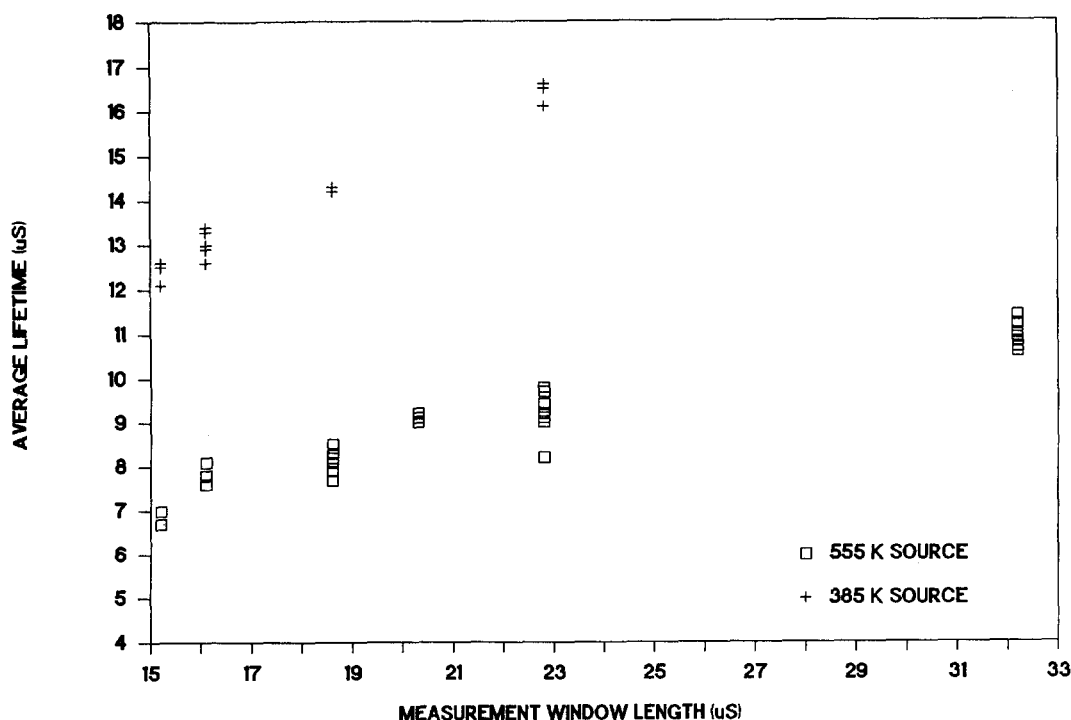


FIG. 1. Measured composite lifetimes ($1/k$) for source temperatures of 385 and 555 K as a function of the experimental measurement time window.

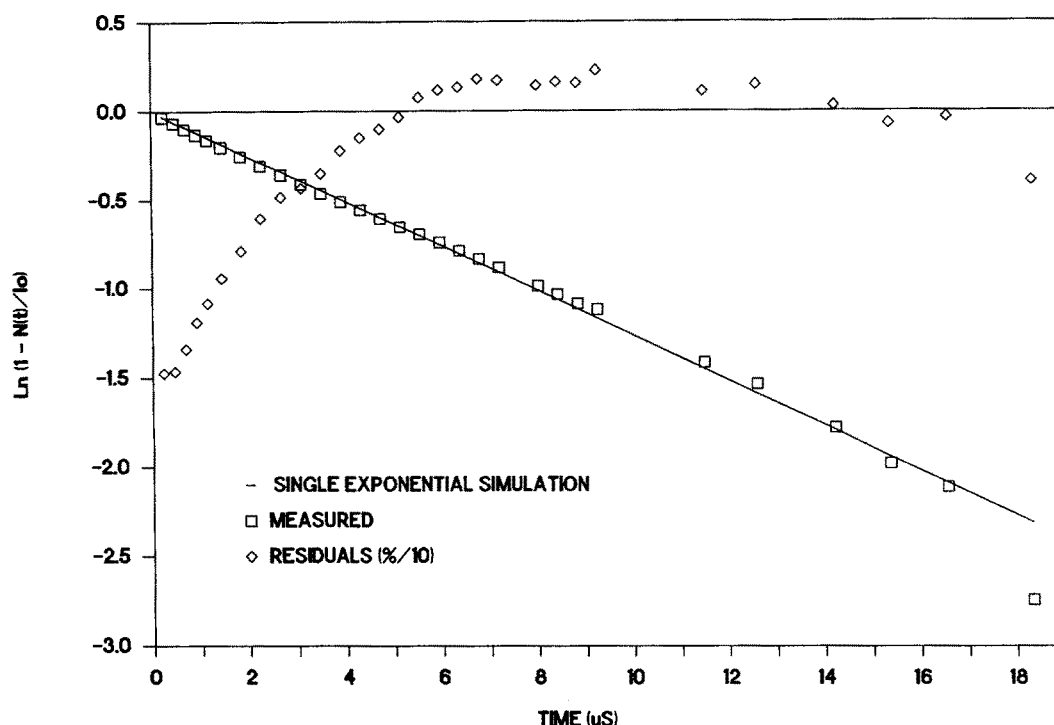


FIG. 2. Measured autoneutralized SF_6^- production rate compared to the calculated rate assuming a single exponential process along with the residuals (simulated — measured in % divided by 10 for presentation clarity) for a 555 K source temperature (Re filament).

Our previous measurements and analysis had indicated that, at a minimum three exponential components were needed to describe the data over the full temperature and observation window ranges. This assumes that there are unique states, adequately separated as to appear distinct within the observation time window, and that a change in the composite lifetime is the result of a change in the distribution of the population densities of the individual states. If this is the case then the data for a variety of observation time windows and source temperatures can be described by a unique set of states (lifetimes) with varying intensities (I_n 's).

Adopting this hypothesis the data has been analyzed by varying the combination of lifetimes and intensities to determine the lifetimes that best predict the full data set.

Figure 3 shows the data of Fig. 2 modeled with a three component exponential, note that the residuals now all fall within $\sim 1\%$ of the measured data. The lifetimes used were 3.0, 12.6, and 23 μs . These lifetimes were determined to be optimum after many combinations were tested against the data for both source temperatures and the full range of observation time windows. Since the observation time window is restricted to a maximum of $\sim 32 \mu\text{s}$ in our apparatus the

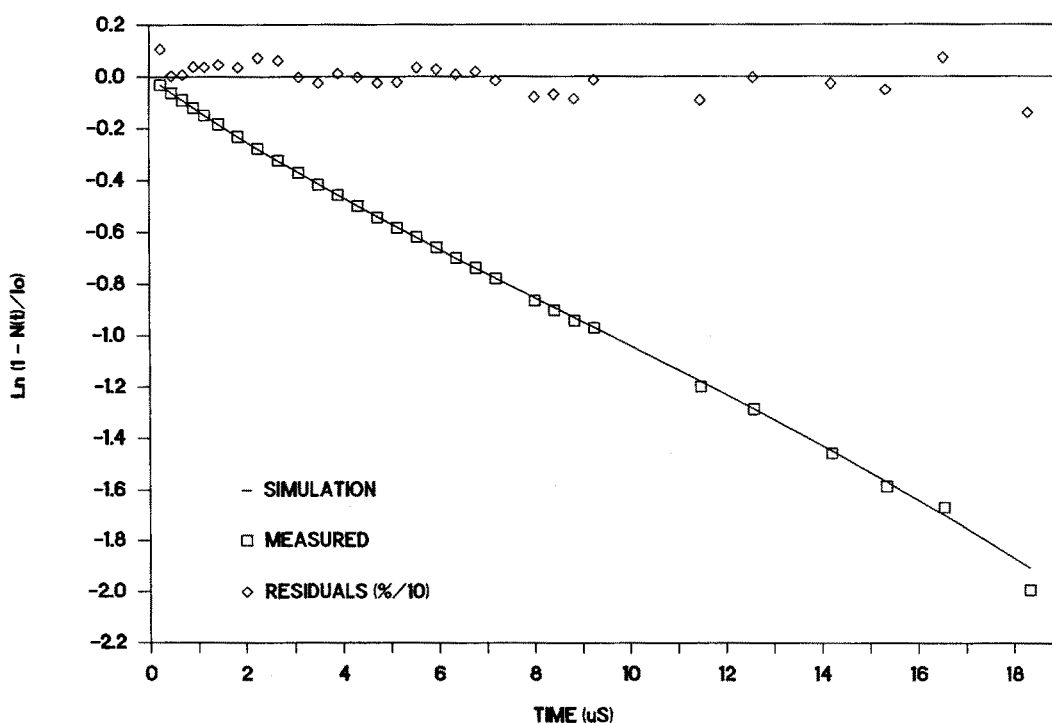


FIG. 3. Measured autoneutralized SF_6^- production rate (same as Fig. 2) compared to the calculated rate using a three component exponential with lifetimes of 3.0, 12.6, and 23 μs .

precision with which the longer lived (12 and 23 μs) states can be determined is quite limited. Figure 4 illustrates the uncertainty in determining the lifetime of the longer lived state. The residuals for models using 23 and 35 μs lifetimes for the longest lived state are essentially identical, neither one could be judged better than the other (although the 18 μs lifetime is obviously too short). This uncertainty was expected and is a limitation of the experimental system since the observation window was only on the order of one lifetime. However, for the short lived component the observation window spans many lifetimes, making it possible to measure this with much better precision. Figure 5 shows the effects on the residuals, again using the same data as Fig. 2, of varying the short lived component lifetime by $\pm 25\%$ from 3.0 μs . It is clear that the analysis is quite sensitive to the short lived lifetime and that the degradation in the quality of fit for a $\pm 25\%$ change is readily apparent. This sensitivity is also present for the lower source temperature data, as shown in Fig. 6, even though there is a lower fraction of short lived component present. The signal to noise ratio (mean to one standard deviation) for the data is ~ 100 , thus the residuals would not be expected to be any better than about $\pm 1\%$. When using the 3.0 μs lifetime for the short lived component the residuals of Figs. 3–6 fall within this expected minimum band. Thus it is possible to determine with reasonable accuracy the lifetime of the short lived state.

To determine the "best" value for the short lived lifetime requires that the lifetimes and the intensities be slowly varied and the resultant residuals examined. Unfortunately, we know of no fitting algorithms for a three component system of exponential transcendental functions (resulting in six degrees of freedom) that can be applied to perform this analysis. The goodness of fit becomes too subjective for simple algorithmic rules to be applied. Thus the fitting must be done

by subjectively judging, based on experience acquired in the process, which parameter to "tweak" to optimize the fit. However, as the fit gets close to optimum one can use the sum of the absolute values of the residuals as a measure of the goodness of fit; the closer the sum is to zero the better the fit. Figure 7 shows the result of using this technique for data for the two different source temperatures. The optimum lifetime (lowest value for sum of residuals) for the 555 K data is at $\sim 2.8 \mu\text{s}$ and for the 385 K data is at $\sim 3.1 \mu\text{s}$. Since the 555 K data contains a significantly higher signal from the short lived component than the 385 K data, the 555 K data is weighted more heavily and the lifetime of the short lived state is estimated to be 2.8 μs ($\pm 10\%$).

This analysis method was applied to the data for the different observation time windows to determine the set of lifetimes that best modeled the complete data set. Using these lifetimes a set of simulations was generated that predicted the neutral intensity as a function of time for the various observation window times. These simulated data sets were then fit with a single exponential and the resulting composite lifetimes of the simulations were compared to the measured composite lifetime for corresponding observation windows. The results, shown in Fig. 8, demonstrate that the triple exponential model does a reasonable job of predicting the response over the full set of observation windows and ion source temperatures. Thus this analysis supports the previous conclusion that, assuming unique and distinct states, a composite of three states can describe the experimental results in a consistent manner. For the time frame of 0–35 μs and source temperature range of 385–555 K the lifetimes that best predicted the data were 2.8, 12.6, and 23 μs . For the high temperature source the relative intensities for these three lifetimes were 0.4 (2.8 μs), 1.0 (12.6 μs), and 0.9 (23 μs). For the low temperature source they were 0.1 (2.8 μs),

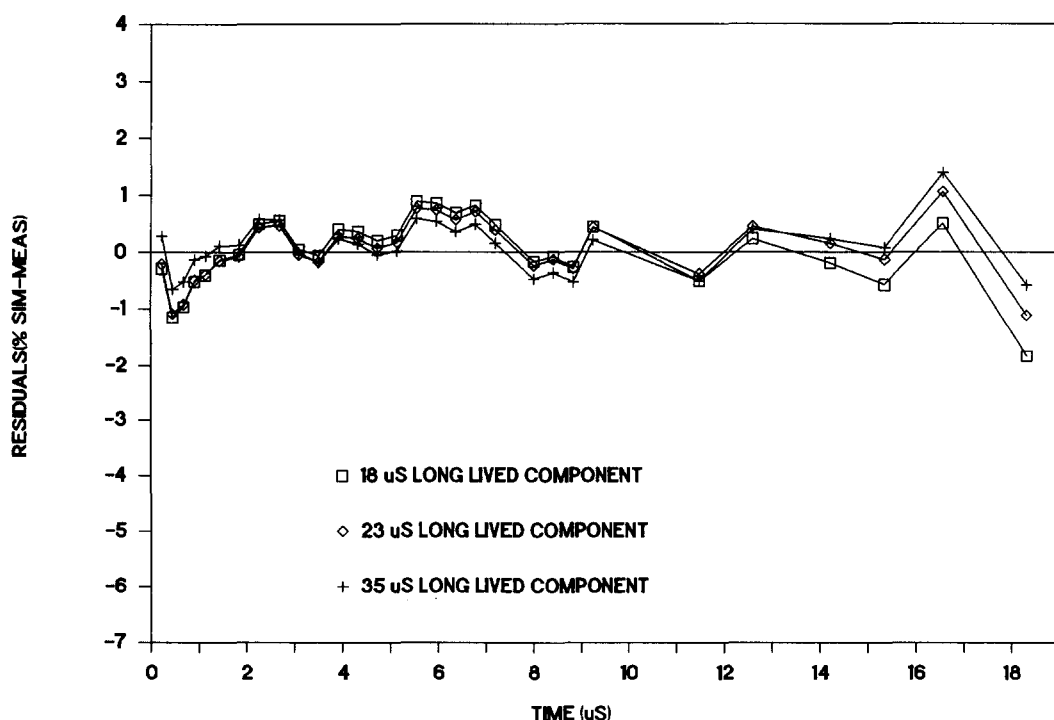


FIG. 4. The effect on the residuals of varying the longer lived state lifetime between 18 and 35 μs while holding the lifetimes of the shorter lived states constant (3.0 and 12.6 μs). This data is for the longest observation window.

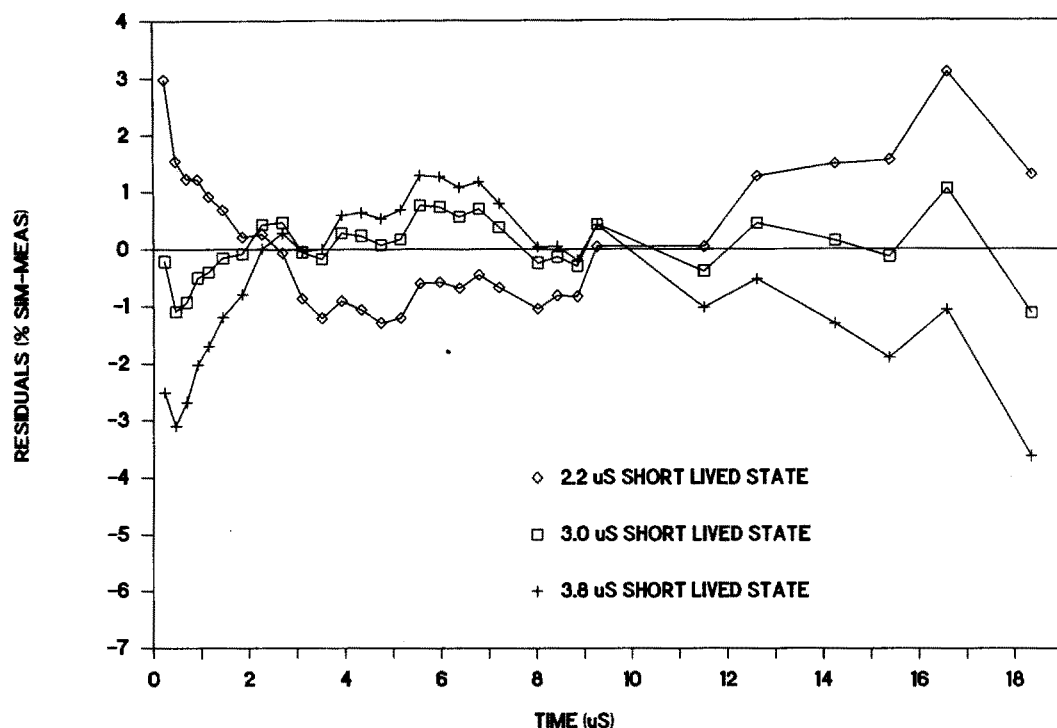


FIG. 5. Residuals for the data of Fig. 2 (555 K source) holding the 12.6 and 23 μs lifetimes constant and varying the short lived state lifetime by $\pm 25\%$ of 3.0 μs .

1.0 (12.6 μs), and 1.6 (23 μs). These population densities were calculated for $t=0$ at the first deflection electrode, which was $\sim 2 \mu\text{s}$ from the point of ion formation. The ratio of the population densities (I_0 's) of the 23 to the 2.8 μs states changes by a factor of 7 over the temperature range. This result, along with the observations of overall beam intensity during the experiments, strongly suggests that the lower temperature source produced significantly fewer ions in the short lived state than the high temperature source, and supports the hypothesis that the distribution of states is tem-

perature dependent, higher temperatures resulting in more highly populated short lived states. An alternate hypothesis for the observed autoneutralization rate is that there is a quasicontinuum of states. This could imply two alternatives: (1) Multiple independent states (more than three) lying close together that can be described by the three component system, as previously shown (the resolution of the existing data precludes definitive identification of the existence of more than three states), or (2) several quasicontinuous states with lifetimes ranging from ~ 2.5 to 8 μs and from 15

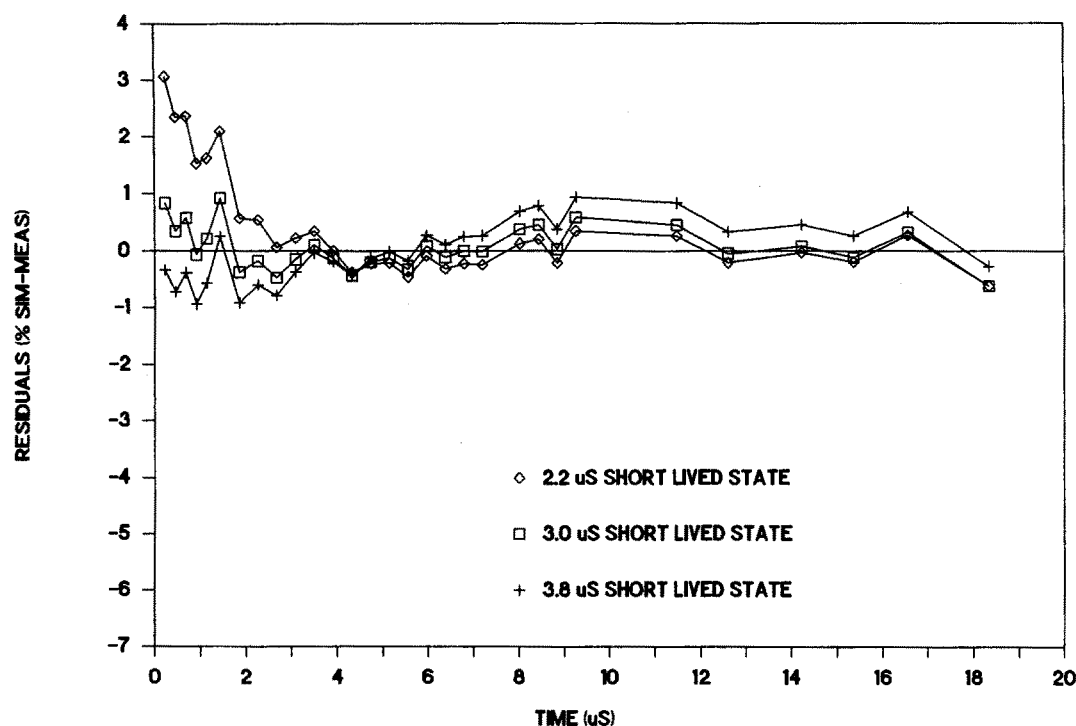


FIG. 6. Residuals for data with a 385 K source temperature using 12.6 and 23 μs for the longer lived states and varying the short lived state lifetime by $\pm 25\%$ of 3.0 μs .

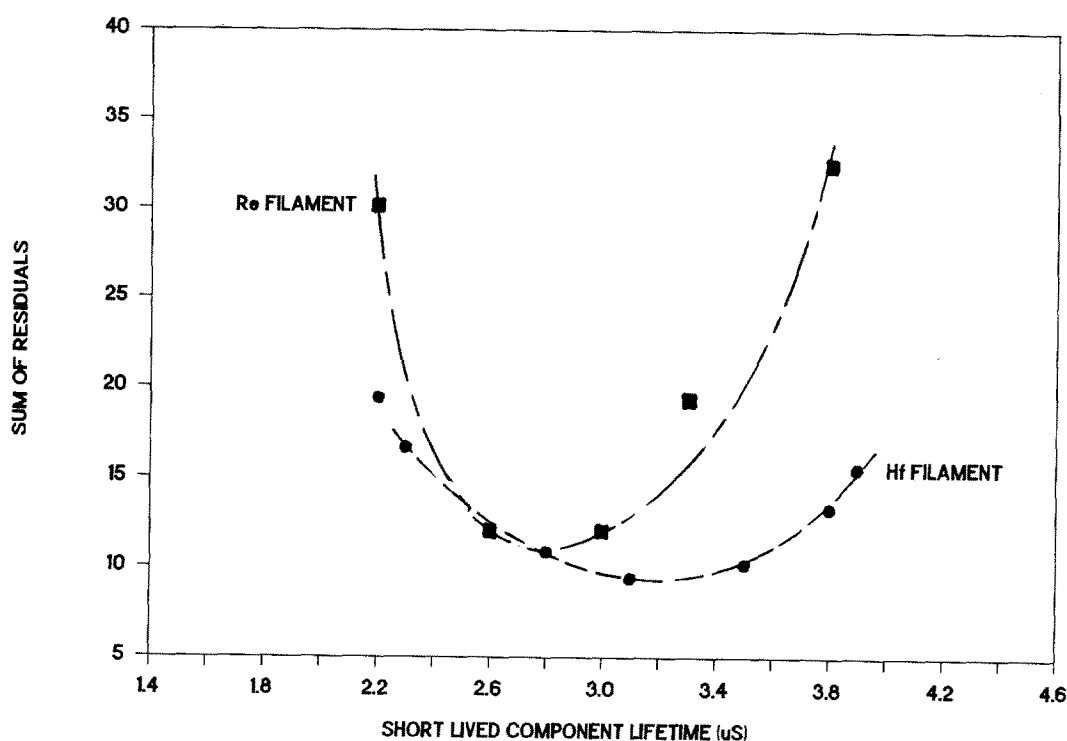


FIG. 7. Sum of the absolute value of the residuals (arbitrary units) as a function of the short lived lifetime for ion source temperatures of 385 and 555 K. The lifetimes of 12.6 and 23 μs for the other two states were held constant.

to 30 μs . Both alternatives can be shown to be consistent with the data, although neither can be shown to be an exclusive solution.

Figures 9 and 10 show the results of modeling the process as a two component exponential (a single component model does not adequately predict the data) in which the lifetimes can vary as a function of source temperature. In Fig. 9 (source temperature of 555 K) the residuals for two different (optimized) sets of lifetimes are compared for different observation windows. There is no significant difference, both the double exponential and triple exponential models perform comparably in predicting the data. Figure 10 presents the same type of analysis for the low temperature source, in this case the double exponential model performs slightly better than the triple exponential at times beyond $\sim 14 \mu\text{s}$. Note that for the 555 K temperature data the optimum lifetimes are 2.8 and 15 μs while for the 385 K data they are 7 and 30 μs . The 7 and 30 μs lifetimes do not adequately predict the 555 K data, as shown in Fig. 11. The 2.8 and 15 μs lifetimes do work reasonably well for the 385 K data because the 2.8 μs component is so small (only 2%) and the 15 μs lifetime is very near the composite lifetime (14.5 μs). However note that the double exponential residual curve retains the bowed shape representative of the composite model and that the triple exponential model overcomes this problem. Thus the analysis indicates that: (1) it is possible to model the process by assuming two independent sets of lifetimes for the different source temperatures, and that, (2) the models (lifetimes) are not interchangeable. This is consistent with an hypothesis suggesting two independently excited states, each having a quasicontinuum. The shorter lived quasicontinuum would span lifetimes in the range of 2.8 to 7 μs , and the longer lived quasicontinuum would span lifetimes in the range of 15 to 30 μs . Taking this one step further this could

be described as a single continuum with two maximums in population density that shift with temperature. Unfortunately the data does not permit any one of these possible alternatives to be clearly distinguished as the most probable.

In summary the analyses indicate that there must be multiple states, either independent or along a quasicontinuum, that autoneutralize at different rates, and that one of these states is short lived with a lifetime of $\sim 3 \mu\text{s}$. More complete knowledge of the various energy levels of the anion and molecule is needed to conclusively determine the number of states that participate in the autoneutralization process.

It may be possible to elucidate this system more fully if one could achieve a more homogeneous gas temperature within the ion source. The ion sources used to date have generated the ions in a region of extremely high thermal gradients. The electron emitting filament (which is also the heat supply to the source) operates at between 1600 and 2300 K and the bulk of the source in the ion formation region is between 350 and 560 K. Thus the gas in the ion formation region has a wide range of thermal energies depending upon how long it spends in the source before capturing an electron and its recent collision history. This is expected to result in a broad distribution of internal energies which is inconsistent with assignment of a specific (single) temperature. Since the internal molecular energy prior to electron capture is thought to control the autoneutralization rate, this broad distribution results in the multiple lifetime behavior seen in the data. If the internal energy spread of the ions could be limited by providing a narrow temperature range in the ion source it may be possible to distinguish whether the process is a quasicontinuum or contains more distinct and separated states.

Our earlier studies¹ showed that the population distri-

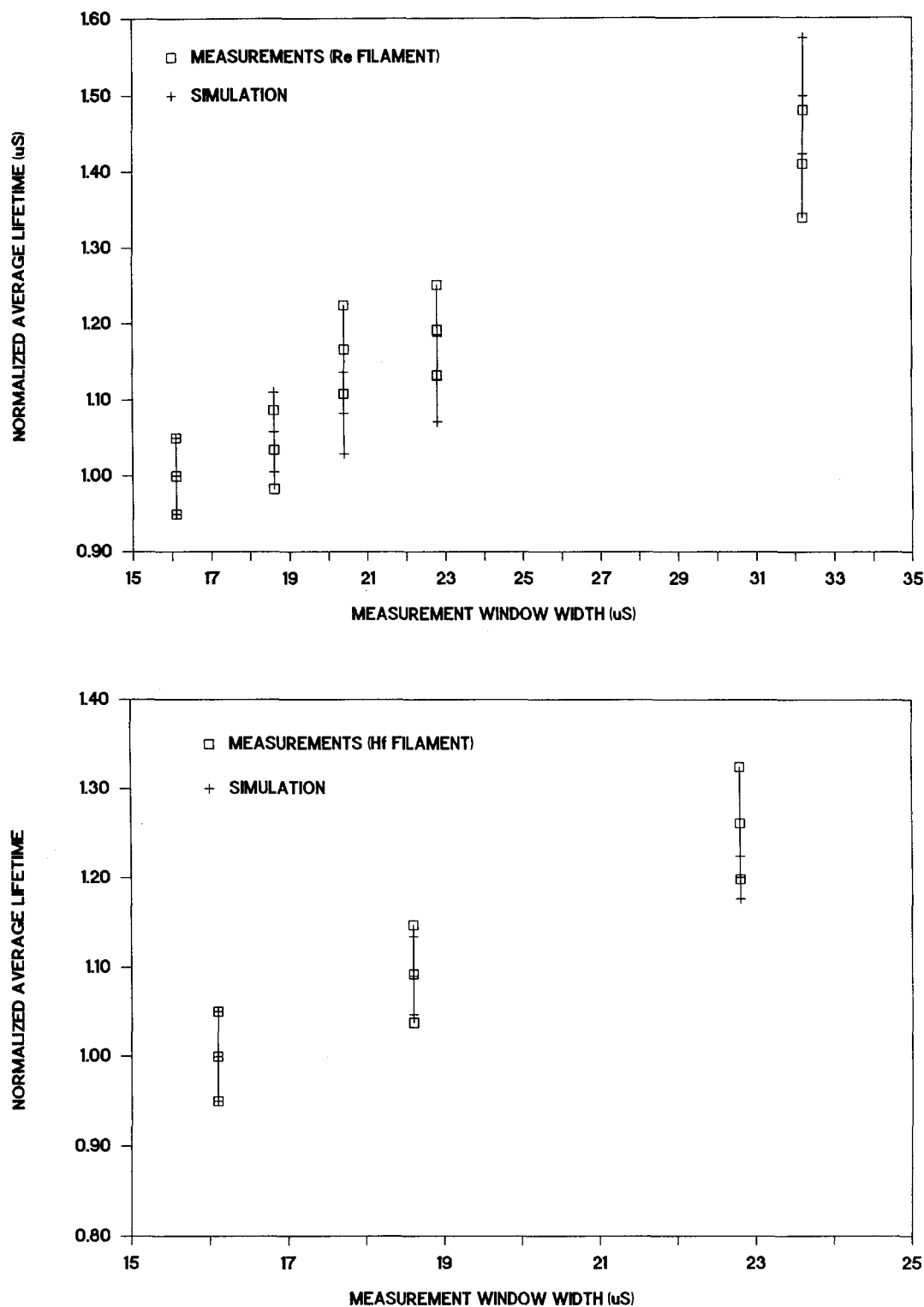


FIG. 8. Composite lifetimes (single exponential) for simulated data (crosses) produced with 2.8, 12.6, and 23 μs lifetimes for various measurement windows compared to the measured composite lifetimes (boxes) for 555 K source (upper plot) and 375 K source (lower plot). Results normalized to the 16 μs window values.

bution of autoneutralizing states was dependent on the bulk temperature of the ion source housing. If one assumes that (1) the majority of the ions are at the source bulk temperature when formed and that (2) the population densities follow a Boltzmann distribution, then the ratio of the population densities at the two source temperatures can be used to calculate the ΔE for these states. The ratio of the populations N_m and N_n of two states at a temperature T is given by⁷

$$N_m/N_n = \exp(-\Delta E/kT), \quad (3)$$

where k is the Boltzmann constant. The ratios of the measured relative populations for the 23 and the 2.8 μs states at ~ 350 and ~ 550 K (corrected to t_0 = ion formation point) are 0.12 and 0.83, respectively. The ratio of these two ratios, $[N_m/N_n]_{T_2}/[N_m/N_n]_{T_1}$ is ~ 7 . This corresponds to a ΔE of 0.17 eV ($\sim 1400 \text{ cm}^{-1}$), which is in the range typical for

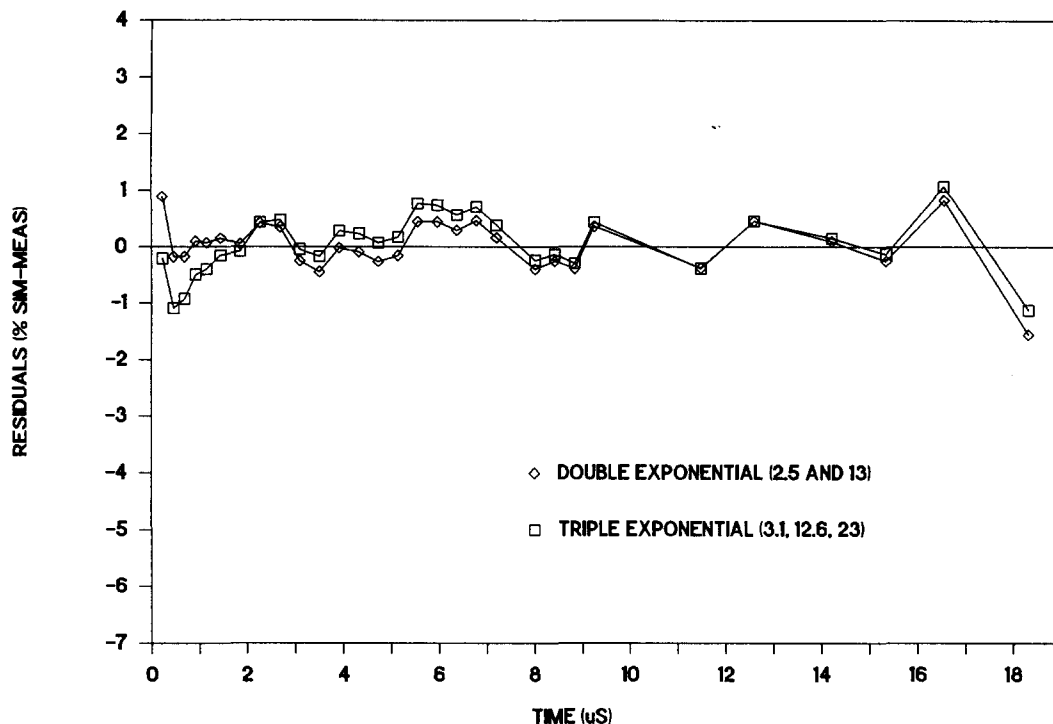
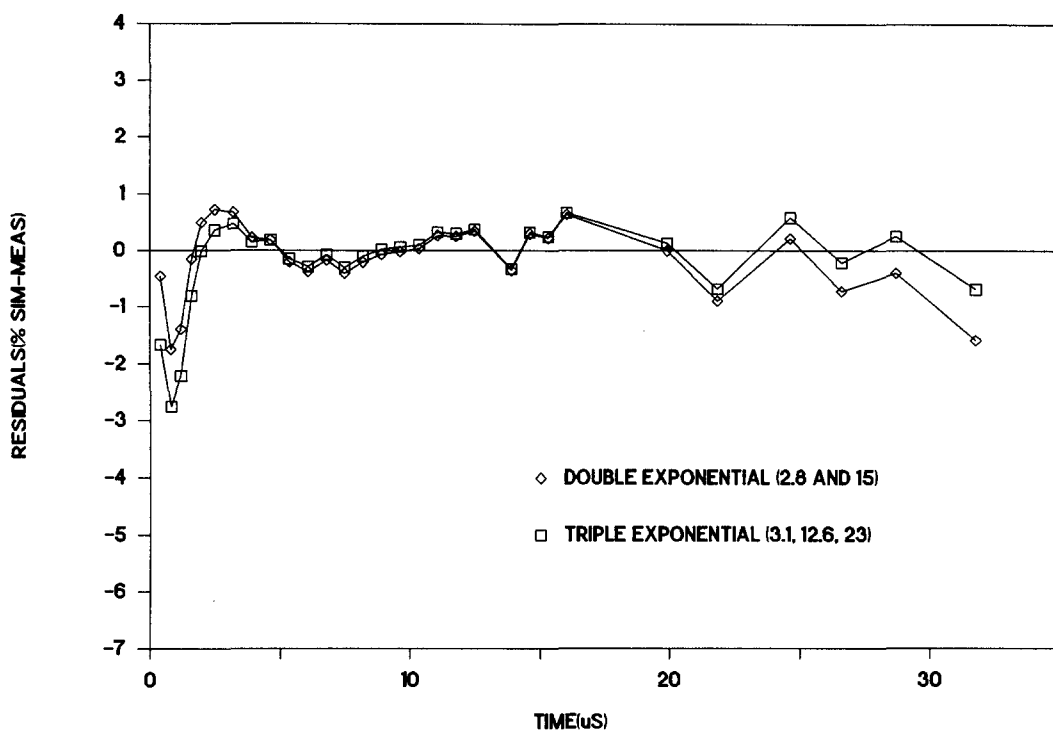


FIG. 9. Comparison of the residuals for a triple and double exponential model for 555 K source data for two observation windows.



vibrational transitions in polyatomic molecules. Thus the data is consistent with an hypothesis suggesting the autoneutralization lifetimes are controlled by the vibrational states of the SF_6^- anions.

CONCLUSIONS

Autoneutralization lifetimes of the SF_6^- anion have been measured for the time window of 2 to 38 μs from ion

formation with particular emphasis on refining the measurement of the short lived component. The results indicate that, for ion source temperatures of ~ 550 K, the short lived component lifetime is $2.8 \pm 0.3 \mu\text{s}$. It has been shown that the data support at least two interpretations of the autoneutralization process: (1) there are three or more distinct states (lifetimes) involved or, (2) there are two (or more) quasi-continua. If there are distinct states then there must be at

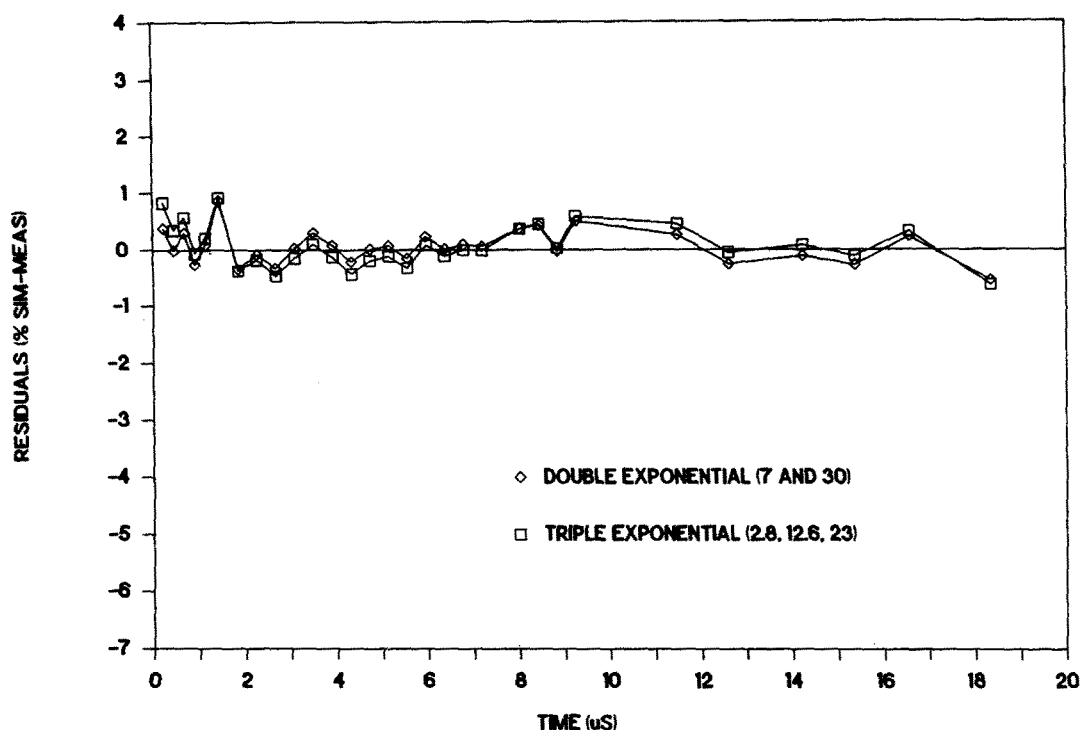
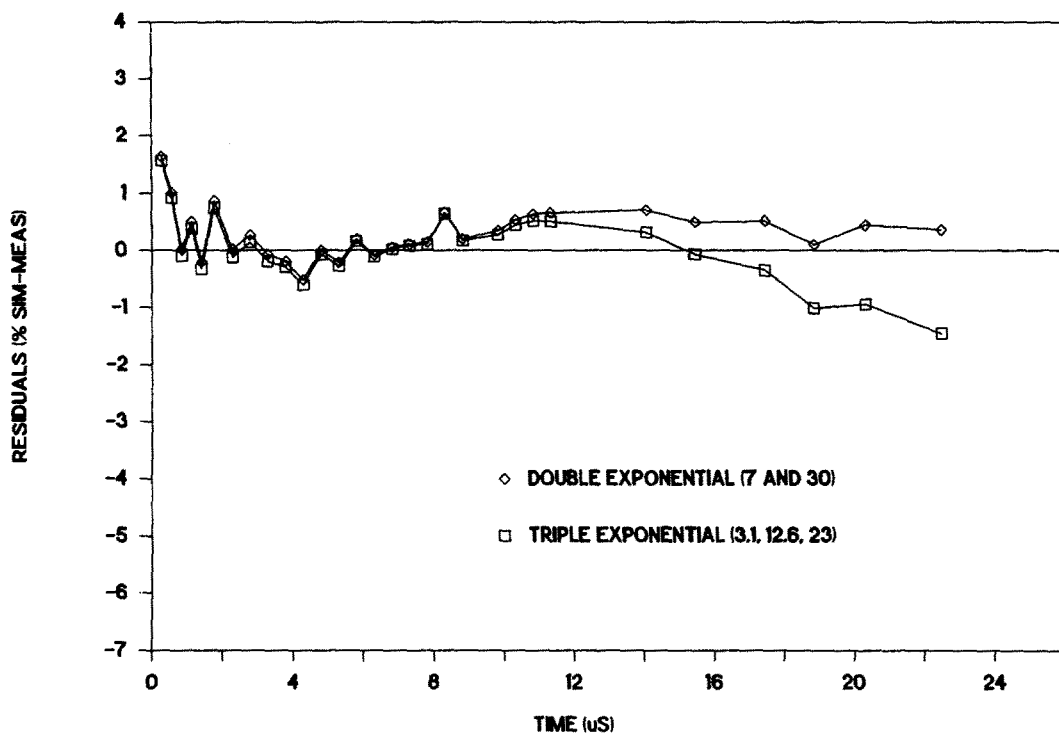


FIG. 10. Comparison of the residuals for a triple and double exponential model for 385 K source data for two observation windows.



least three and, if there are only three, they have lifetimes of ~ 2.8 , 12.6 , and $23 \mu\text{s}$. If there are more than three within this range (~ 2 to $40 \mu\text{s}$) the present data is insufficient to differentiate between them. If there are two quasicontinua then the lifetimes must vary from 2.8 to $7 \mu\text{s}$ for one and from 15 to $30 \mu\text{s}$ for the second. The high temperature

gradients within the ion source employed in these measurements, which resulted in a wide spread in molecular internal energies, prohibits a definitive determination of which of these two alternatives is correct. Measurements of the vibrational and rotational energy levels of the SF_6 molecule and anion are needed to conclusively address this issue.

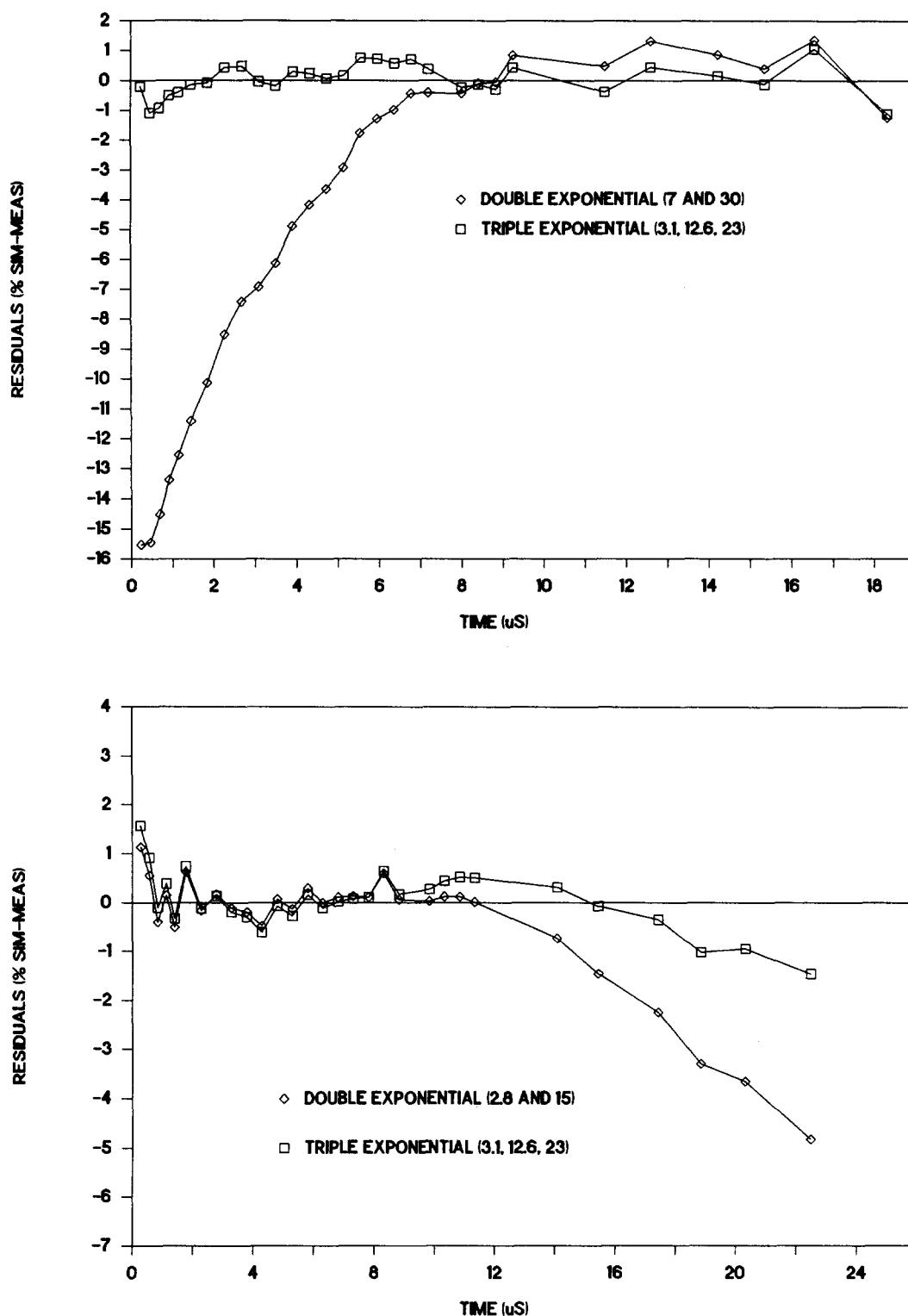


FIG. 11. Comparison of the residuals for triple and double exponential models. Upper graph is for 555 K source data using the lifetimes optimized for the 385 K data and lower graph is for the 385 K source data using lifetimes optimized for the 555 K source data.

ACKNOWLEDGMENTS

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¹J. E. Delmore and A. D. Appelhans, *J. Chem. Phys.* **84**, 6238 (1986).

²R. W. Odom, D. L. Smith, and J. H. Futrell, *J. Phys. B* **8**, 1349 (1975).

³A. D. Appelhans, J. E. Delmore, and D. A. Dahl, *Anal. Chem.* **59**, 13, 1685 (1987).

⁴J. E. Delmore, *Int. J. Mass. Spectrom. Ion Phys.* **51**, 191 (1983).

⁵(a) D. A. Dahl and J. E. Delmore, *Proceedings of the 35th American Society Mass Spectrometry*, Denver (1987); (b) *SIMION PC/AT User's Manual Version 3.0*, EGG-CS-7233 Rev. 1 (1987).

⁶P. S. Drzaic and J. I. Brauman, *J. Am. Chem. Soc.* **104**, 13 (1982).

⁷J. M. Hollas, *High Resolution Spectroscopy* (Butterworth, Washington, D.C., 1982), p. 38.