Laser kinetic spectroscopy of elementary gas phase processes

Curt Wittig

(Depts. of E. E., Physics, and Chemistry, University of Southern California)
University Park, Los Angeles, CA 90007, USA

In this paper, experiments will be described in which elementary gas phase processes are studied using various forms of laser kinetic spectroscopy. The generality of the techniques will be discussed, and specific examples will be used in order to punctuate the discussion.

With pulsed lasers, it is possible to prepare large concentrations of free radicals in a few ns (using UV photolysis) on 100's of ns (using IR photolysis). These species can be monitored using laser induced fluorescence (LIF), and the time evolution of the free radical of interest can be obtained straightforwardly. Products can be monitored by LIF, and also chemiluminescence when products are electronically excited. Spectra can be taken with an optical multielement array which has the ability to take an entire spectrum on a single shot.

Our experimental results on the chemistry of molecular carbon will be reviewed, as these results were all obtained using the above experimental arrangement. We have been able to unravel the detailed, state selective chemistry of gas phase C_2 ($X^1\Sigma_g^+$), C_2 ($a^3\Pi_u$), and C_3 ($X^1\Sigma_g^+$), and these experiments will be discussed in detail. We show that (a) C_2 ($X^1\Sigma_g^+$) and C_2 ($a^3\Pi_u$) react quite differently in general even though they are separated by only 610 cm^{-1}, (b) C_3 ($\tilde{X}^1\Sigma_g^+$) is very unreactive at low temperatures, and (c) the specificity of the entrance channel is preserved as selective electronic excitation in products.

基本气相过程的激光动力光谱学

Curt Wittig

(南加州大学电气工程系,物理系,化学系)

本文描述了用各种形式的动力光谱术研究基本气相过程的实验。讨论了这种技术的普遍性以及举了一些特例以加强这种讨论。

利用脉冲激光器有可能在几个毫微秒(利用紫外光解)以及几百个毫微秒(利用红外光解)的时间内产生高浓度的自由基。这些产物可以通过激光感应的荧光来监测，而且也可以直接得到我们所需的自由基随时间的变化过程。产物可以用激光感应的荧光来监测；当产物是电子激发时也可以用化学发光来监测。利用光学多元阵列可以得到这些光谱，这种多元阵列利用一次照射就能获得整个光谱。

评述了我们对于分子碳化学的实验结果，这些结果就是用上述的实验装置取得的。我们已经能够阐明气相 C_2 ($X^1\Sigma_g^+$)，C_2 ($a^3\Pi_u$)以及 C_3($\tilde{X}^1\Sigma_g^+$)详细的状态选择的化学，并对这些实验作详细的讨论。我们得到的结果是：(a) C_2($X^1\Sigma_g^+$)和 C_2($a^3\Pi_u$) 的反应一般是极为不同的，尽管它们只差开 610 厘米$^{-1}$；(b) C_3 ($\tilde{X}^1\Sigma_g^+$) 在低温下是十分不活泼的；(c)在产物中，输入通道的特征是作为选择性的电子激发而被保持着的。