

Figure 2. Equilibrium binding experiments with HQD (●) and its structural analog HQD-CB (▲). Substrate remained in solution as a function of the mass of added polymer P₆E is presented.

References

- (a) Wulff, G. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1812. (b) Davis, M. E.; Katz, A.; Ahmad, W. R. *Chem. Mater.* **1996**, *8*, 1820. (c) Muldoon, M. T.; Stanker, L. H. *Chem. Ind.* **1996**, March 8, 204.
- (a) Beach, J. V.; Shea, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 379. (b) Karmalkar, R. N.; Kulkarni, M. G.; Mashelkar, R. A. *Macromolecules* **1996**, *29*, 1366. (c) Robinson, D. K.; Mosbach, K. *J. Chem. Soc., Chem. Comm.* **1989**, 969.
- (a) Cooper, M. E.; Hoag, B. P.; Gin, D. L. *Polym. Prep.* **1997**, *38*, 209. (b) Chen, C.-T.; Chen, G.; Guan, Z.; Lee, D.; Arnold, F. H. *Polym. Prep.* **1996**, *37*, 216.
- Vlatakis, G.; Andersson, L. I.; Muller, R.; Mosbach, K. *Nature* **1993**, *361*, 645.
- (a) Sellergren, B. *J. Chromatogr. A.* **1994**, *673*, 133. (b) Fischer, L.; Muller, R.; Ekberg, B.; Mosbach, K. *J. Am. Chem. Soc.* **1991**, *113*, 9358. (c) Wulff, G.; Schauhoff, S. *J. Org. Chem.* **1991**, *56*, 395.
- (a) Wynberg, H.; Staring, E. G. J. *J. Am. Chem. Soc.* **1982**, *104*, 166. (b) Herman, K.; Wynberg, H. *J. Org. Chem.* **1979**, *44*, 2238.

New Nozzle System of the Corona Excited Supersonic Expansion

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Received September 22, 1997

The supersonic free jet expansion of molecules in the gas phase has become an important spectroscopic tool for the observation of rotationally cooled vibronic spectra of large molecules at low temperature.¹⁻³ Stable molecules having appreciable vapor pressures in the gas mixture of high pressure carrier gas are expanded into the vacuum side through small hole to obtain low rotational temperature and reduced Doppler broadening as well as van der Waals cluster. This technique has been routinely employed for the spectroscopic study of stable molecules and clusters generated from stable molecules. Methods have been also developed for the transient molecules such as radicals and ions in free jet.

Engelking⁴ has developed the nozzle system of the corona excited supersonic expansion, in which the transient molecules at the excited state were produced in free jet from stable precursor by electron impact. The nozzle was made by a simple method. A small glass tube was closed down at one end by flame heating and then ground back until the nozzle opening of the appropriate dimension is formed. The metal anode sits just behind the nozzle opening on the high pressure side by 3-5 nozzle diameter, thus allowing expansion after excitation of the molecules. Also, the efficient collisional vibrational cooling at the nozzle throat simplifies the vibronic emission spectrum by reducing the

intensity of hot bands originating from the vibrationally excited states of the excited electronic state. Thus, the emission spectrum is similar to the dispersed fluorescence spectra observed by exciting the origin band. This type of nozzle has been widely used for the observation of vibronic emission spectra of stable molecules⁵ and unstable species.⁶⁻¹¹ However, this substantially deteriorates the stability of discharge when heavy organic compounds were used as precursors. The messy fragments generated from the precursor by electron impact easily clog the small throat of the nozzle. Thus, with this type of nozzle, it was extremely difficult to obtain the vibronic emission spectra of large molecules showing the well-resolved rotational contours.

In the spectroscopic studies of vibronic transition, the rotational constants and symmetry of large molecules at a given state can be determined from the analysis of rotational contour of each vibronic band.^{8,12,13} In order to observe the vibronic emission spectrum showing the well-resolved rotational contour, highly stable discharge condition should be maintained in a corona excited supersonic expansion, since the ratio of signal to noise of the spectrum is usually limited by the fluctuation of the discharge current which is also affected by the amount of the gas flow through the throat of nozzle.

Recently, we have improved the stability of the discharge

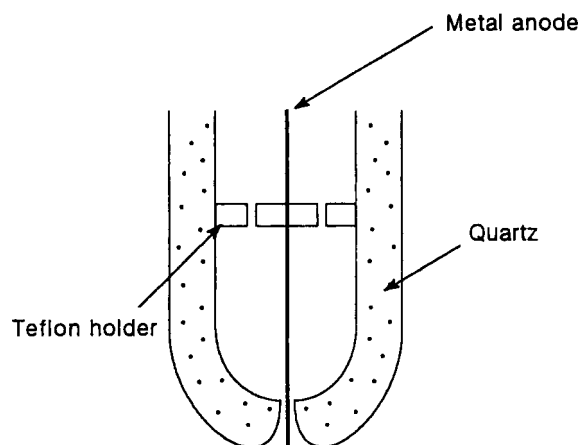


Figure 1. The schematic diagram of the nozzle system developed in this work. The metal tip used as an anode is exposed outside the nozzle throat.

by employing the new nozzle system developed in this laboratory. Figure 1 shows the schematic diagram of the nozzle system which is similar to that developed by Engelking and coworkers.^{4,14} The thick wall quartz tube of 12.7 mm in outer diameter was narrowed at one end by flame heating until the nozzle opening of the appropriate dimension formed. A long sharpened metal rod was inserted through a few of teflon holders into the nozzle throat and fixed in the center of the tube. The teflon holder which is the most important thing in this development was made from 3 mm thickness of teflon disc of which diameter is exactly the same as the inner diameter of the nozzle tube. There are one main hole in the center for the metal rod and several small holes for the gas flow. The nozzle tube was linked to the threaded adaptor (Ace glass model 5027-05). The metal tip of anode was positioned outside the nozzle opening on the vacuum side while it was placed inside the nozzle opening in the original Engelking nozzle. Although the length of metal tip exposed to the vacuum side is less than 0.5 mm, it substantially changes the mechanism by allowing excitation after expansion, leaving little amount of clogging in the throat compared to the original nozzle. Also, it shows better control of discharge condition to generate desirable fragments from the precursor. However, it was found that the metal tip should be centered in the nozzle throat to prevent the jet flow from deflection which considerably reduces the stability of discharge over a long period. The new nozzle can be easily switched into the Engelking type nozzle by pulling the anode up inside the nozzle throat.

In our previous paper,¹⁰ we have reported the observation of vibronic emission spectrum of the *p*-xylyl radical in the transition of $1^2A_2 \rightarrow 1^2B_2$ taken at resolution of 2.0 cm^{-1} in a corona excited supersonic expansion. Among the vibronic bands observed, the $6a_1^0$ and $6b_1^0$ bands show strong intensity as well as the origin band and the 1_1^0 band. However, the assignment of the normal vibrational modes 6a and 6b was ambiguous due to the proximity of the transition frequencies though they have quite different symmetry in the spectrum.¹⁵ Thus, the accurate vibrational assignment can be determined from the analysis of the well-resolved rotational contour of the band.

In order to obtain the vibronic emission spectrum show-

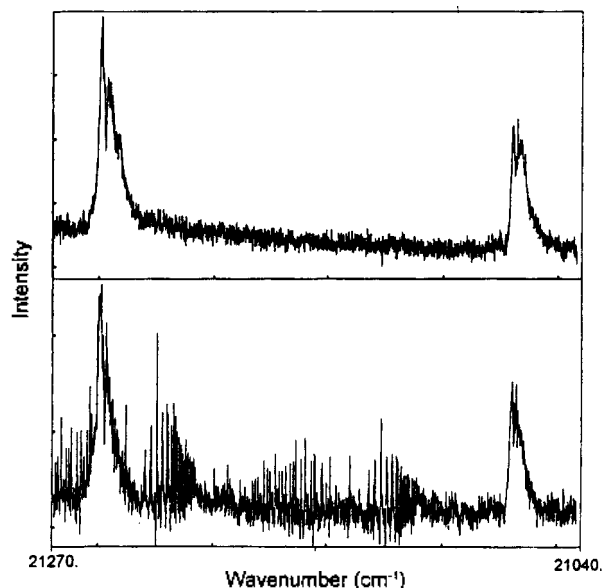


Figure 2. A comparison of the vibronic emission spectrum showing the $6a_1^0$ and $6b_1^0$ bands. The lower spectrum was obtained with the original Engelking nozzle while the upper one was observed with the new nozzle developed in this work. Other experimental conditions are the same for both spectra. The sharp lines in the lower spectrum may be attributed to the C_2 molecules generated from the corona discharge of the precursor. Two bands in the upper spectrum show different bandshapes.

ing a fairly well-resolved rotational contour, we have generated the *p*-xylyl radical with a buffer gas He in free jet from *p*-xylene in a corona excited supersonic expansion using the experimental apparatus and conditions similar to those reported previously.¹⁰ The emission was recorded with a Fourier transform spectrometer (Bruker IFS 120HR) equipped with PMT detector (Hamamatsu R106UH). A total of 100 scans have been added together over 2 hrs. to obtain the spectrum shown in Figure 2 which was taken at resolution of 0.1 cm^{-1} . In this experiment, we have employed a narrow band (10 nm bandwidth) optical interference filter centered at 470 nm to improve the signal to noise ratio of the spectrum. In Figure 2, the lower spectrum was obtained with the original Engelking nozzle while the upper spectrum was taken with the nozzle developed in this work. Using new nozzle, we have found that the ratio of signal to noise of spectrum was improved by a factor of 7. From the upper spectrum, we can clearly see the different bandshapes at 21241 cm^{-1} from at 21062 cm^{-1} suggesting both bands have different symmetry. The 1_1^0 and origin bands were also observed using different optical filters at the frequencies reported previously.^{6,16} We have taken the low resolution survey spectrum of the *p*-xylyl radical, in which the absence of hot bands with observable intensity indicates the efficient collisional cooling of the vibrationally excited molecules at the excited electronic state. The analysis and assignments of the rotational band contour will be published elsewhere.

In summary, we have developed new nozzle system which is useful for the rotationally well-resolved vibronic emission spectra of large molecules. The nozzle exhibits improved signal to noise ratio in the vibronic emission spec-

trum of the p-xylyl radical compared with that obtained using the original Engelking type nozzle. From the survey spectrum, we have found that the collisional vibrational cooling is efficient at the exit of the nozzle throat.

Acknowledgements. The present study was supported by the matching fund programs of the Research Institute for Basic Sciences, Pusan National University, Korea, 1997, Project No. RIBS-PNU-97-303. The author thanks to The Ohio State University for allowance to use the Fourier transform spectrometer.

References

1. Miller, T. A. *Science* **1984**, *223*, 545.
2. Smalley, R. E.; Wharton, L.; Levy, D. H. *J. Chem. Phys.* **1975**, *63*, 4977.
3. Smalley, R. E.; Ramakrishna, B. L.; Levy, D. H.; Wharton, L. *J. Chem. Phys.* **1974**, *61*, 4363.
4. Engelking, P. C. *Rev. Sci. Instrum.* **1986**, *57*, 2274.
5. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 262.
6. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*,

277.

7. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1989**, *137*, 13.
8. Suh, M. H.; Lee, S. K.; Rehfuss, B. D.; Miller, T. A.; Bondybey, V. E. *J. Phys. Chem.* **1991**, *95*, 2727.
9. Brazier, C. R. *J. Mol. Spectrosc.* **1996**, *177*, 90.
10. Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1995**, *16*, 1089.
11. Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *11*, 749.
12. Choi, I. S.; Han, M. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 882.
13. Hollas, J. M. *Electronic Spectra of Large Molecules; Molecular Spectroscopy*; Specialist Periodical Reports, The Chemical Society, 1973; Vol. 1.
14. Drooge, A. T.; Engelking, P. C. *Chem. Phys. Lett.* **1983**, *96*, 316.
15. Carrick, P. G.; Selco, J. I. *J. Mol. Spectrosc.* **1990**, *139*, 449.
16. Charlton, T. R.; Thrush, B. A. *Chem. Phys. Lett.* **1986**, *125*, 547.

The Effect of Alkali Metal Ions on Acyl-Transfer Reactions: Unusually High Na⁺ Ion Selectivity in the Reaction of 8-(5-Nitroquinolyl) Benzoate with Alkali Metal Ethoxides in Ethanol

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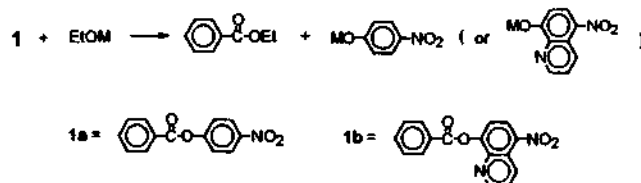
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The effect of metal ions on acyl-transfer reactions has been extensively studied due to the importance in biological processes.¹⁻⁷ However, most studies have been focused on divalent metal ions such as Ni²⁺, Zn²⁺, Cu²⁺, etc.^{1,2} The study of alkali metal ions has not been much investigated but initiated only recently.³⁻⁷ Bunce and his coworkers have found that alkali metal ions behave as a catalyst in the reaction of alkali metal ethoxides (EtOM) with *p*-nitrophenyl diphenylphosphinate (PNPDPP) in ethanol (EtOH).^{3a} The catalytic effect was found to increase with increasing the charge density of alkali metal ions (e.g., K⁺ < Na⁺ < Li⁺).^{3a} However, on the contrary, alkali metal ions have been reported to act as an inhibitor in the reaction of PNPDPP with alkali metal aryloxides (ArOM) in EtOH, and the inhibiting effect increases with increasing the charge density of alkali metal ions.^{3a} Interestingly, in the reaction of EtOM with *p*-nitrophenyl benzenesulfonate (PNPBS) in EtOH, Li⁺ ion behaved as an inhibitor while K⁺ and Na⁺ exhibited catalytic effect.^{3b,4b} Therefore, it has been understood that alkali metal ions play as a catalyst or inhibitor in the above nucleophilic substitution reactions depending on the type of substrates (phosphorus vs sulfur centered ester) and nucleophiles (EtO⁻ vs. ArO⁻), and the catalytic or inhibiting

ability is in the order Li⁺ > Na⁺ > K⁺ or K⁺ > Na⁺ > Li⁺.^{3,4}

Recently, we have reported a similar result for the reaction of EtOM with *p*-nitrophenyl 2-furoate (PNPF)^{4d} and 2-thiophenecarboxylate (PNTC)^{4e} in EtOH, i.e., alkali metal ions exhibited catalytic effect and the catalytic ability was in the order K⁺ > Na⁺ > Li⁺. For a more systematic study, we have performed the reaction of EtOM with *p*-nitrophenyl benzoate (**1a**) and 8-(5-nitroquinolyl) benzoate (**1b**) in EtOH. We wish to report unusually high Na⁺ ion selectivity together with the role of alkali metal ions in the present system.



The reactions were followed by monitoring the appearance of the leaving group at 400 nm (**1a**) or 455 nm (**1b**) using a Hitachi U-2000 UV-vis spectrophotometer equipped with a Neslab RTE-110 model constant temperature circulating bath. All the reactions were performed