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May 28, 1998

To: Dr. Hashima Hasan

From: Ted Snow

Subject: "Final" report, grant NAG5-4184 (153 4529)

This report is intended to fill in the blanks in NASA's file system for our lab astro study of molecular ions of astrophysical interest. As usual, there is virtually no connection between the report requirements and the actual progress of the research, because: (a) the funding these days from NASA is usually about a year behind; and (b) for its own reasons, NASA has elected to continually change the grant number for the support for this work, resulting in extra, unnecessary paperwork at both ends (this report is a perfect example).

Grant NAG5-4184 supported the third year of a three-year program of study. An additional year has since been funded, but (against our wishes) under a new grant number (NAG5-6758). Hence we have requested (some months ago!) a no-cost extenstion for grant NAG5-4184, with no response from NASA as yet. Pending the outcome of our request for a no-cost extension to grant NAG5-4184, this memo may be viewed as either a final report or an interim progress report (and in either case is redundant because we provided a full review of our research progress when we proposed a year ago to continue the program).

In order to give NASA what it needs for its files, I attach below the text of the section from our recent proposal to continue this work, in which we describe progress to date, including a large number of publications. Here it is:

III. Previous work

Our initial studies were focused on PAH cations, which appear to be viable candidates as the carriers of the DIBs (Van der Zwet and Allamandola 1985; Léger and d'Hendecourt 1985; Crawford *et al.* 1985), an idea that has been supported by laboratory spectroscopy of PAH cations in inert matrices (Salama and Allamandola 1992a,b; Léger *et al.* 1995). Beginning with the simplest aromatic (benzene; C_6H_6) and moving progressively to larger species (naphthalene, $C_{10}H_8$; pyrene, $C_{16}H_{10}$; and most recently chrysene, $C_{18}H_{12}$), we have been able to derive rate coefficients for reactions with neutral

species that are abundant in the diffuse interstellar medium. Our principal results have been as follows:

First, we found that the reactions of atomic hydrogen dominate over those of other abundant neutrals, for two reasons: (1) hydrogen has larger reaction rate coefficients with PAH^+ than do other neutrals such as N I and O I; and (2) hydrogen is far more abundant than other potential reaction partners (by about a factor of 10^4 in the cases of N I and O I and more for other atoms or simple molecules).

Second, we found that the parent PAH cations quickly migrate to their protonated forms (i.e. the cationic form having one additional hydrogen atom), on timescales more rapid than those for other processes such as electron recombination (but note that the electron recombination rate coefficients are not well known; see our discussion below). The transition to the protonated form also occurs for PAH cations that are initially dehydrogenated, either by the addition of an H_2 molecule (also measured in our experiments) or successive additions of hydrogen atoms. Once in the hydrogenated form, the PAH cations have closed shells and become relatively inert, with very slow reaction rate coefficients for further interaction with the reagents studied.

Thus we conclude that small PAH cations in the diffuse ISM will migrate to their protonated forms and remain there until destroyed by some non-chemical process. This would seem to rule out small PAH cations as carriers of the DIBs, but it is not certain whether this conclusion extends to large PAH cations, to a host of heterocyclic PAH cations, or to those with various kinds of end groups such as aliphatic chains. These possibilities require further study, which is a part of our proposed research program.

Table 1 summarizes our measurements of reaction rate coefficients for the cations of benzene, naphthalene, and pyrene (including dehydrogenated and protonated forms).

Table 1. Measured reaction rate coefficients

Reactants	H_2	H	O	N
Benzene				
$C_6H_5^+$	5.0×10^{-11}	$\sim5\times10^{-11}$		
$C_6H_6^+$	no rxn	2.2×10^{-10}	9.5×10^{-11}	1.2×10^{-10}
$C_6H_7^+$	no rxn	$\sim3\times10^{-12}$		
Naphthalene				
$C_{10}H_7^+$	5.2×10^{-11}	$\sim5\times10^{-11}$	--	--
$C_{10}H_8^+$	no rxn	1.9×10^{-10}	1.0×10^{-10}	2.3×10^{-11}
$C_{10}H_9^+$	no rxn	$\sim4\times10^{-12}$	--	--

Pyrene				
$C_{16}H_9^+$	no rxn	~1.6×10^{-10}	~2×10^{-10}	~3×10^{-11}
$C_{16}H_{10}^+$	no rxn	1.4×10^{-10}	9.5×10^{-11}	1.5×10^{-12}
$C_{16}H_{11}^+$	no rxn	~4×10^{-12}	--	--

The results of our work to date have appeared, or are in the process of appearing, in publications as follows:

Le Page, V., Keheyan, Y., Bierbaum, V. M., and Snow, T. P. 1997, "Chemical Constraints on Organic Cations in the Interstellar Medium", *J. Am. Chem. Soc.*, **119**, 1135

Snow, T. P., Le Page, V., and Bierbaum, V. M. 1998, "The Interstellar Chemistry of PAH Cations", *Nature*, **391**, 259

Le Page, V., Keheyan, Y., Bierbaum, V. M., and Snow, T. P. "Reactions of Cations derived from Naphthalene with Molecules and Atoms of Interstellar Interest," *J. Am. Chem. Soc.*, in preparation.

Le Page, V., Keheyan, Y., Bierbaum, V. M., and Snow, T. P. "Experimental Studies of the Reactions of Pyrene Cation," *J. Am. Chem. Soc.*, in preparation.

Le Page, V., Keheyan, Y., Bierbaum, V. M., and Snow, T. P. "A Model for the Formation and Loss Processes for PAH Cations in the Interstellar Medium," *Astrophysical Journal.*

The papers on naphthalene and pyrene are detailed descriptions of our work on these two species, and will be submitted to the *Journal of the American Chemistry Society*, while the paper on modeling the physics and chemistry of PAH cations in the diffuse ISM will be submitted to the *Astrophysical Journal.* The naphthalene paper is complete and awaits only a final editing before submission; the pyrene paper needs some additional re-writing but is complete; and the modeling paper will require about one additional month of work, but is already in draft form.

Very recently we have obtained measurements of reaction rates for chrysene cation ($C_{18}H_{12}^+$), with very similar results to those obtained previously, suggesting that the trend continues toward larger PAH cations. We are currently studying the reactions of coronene ($C_{24}H_{12}^+$).

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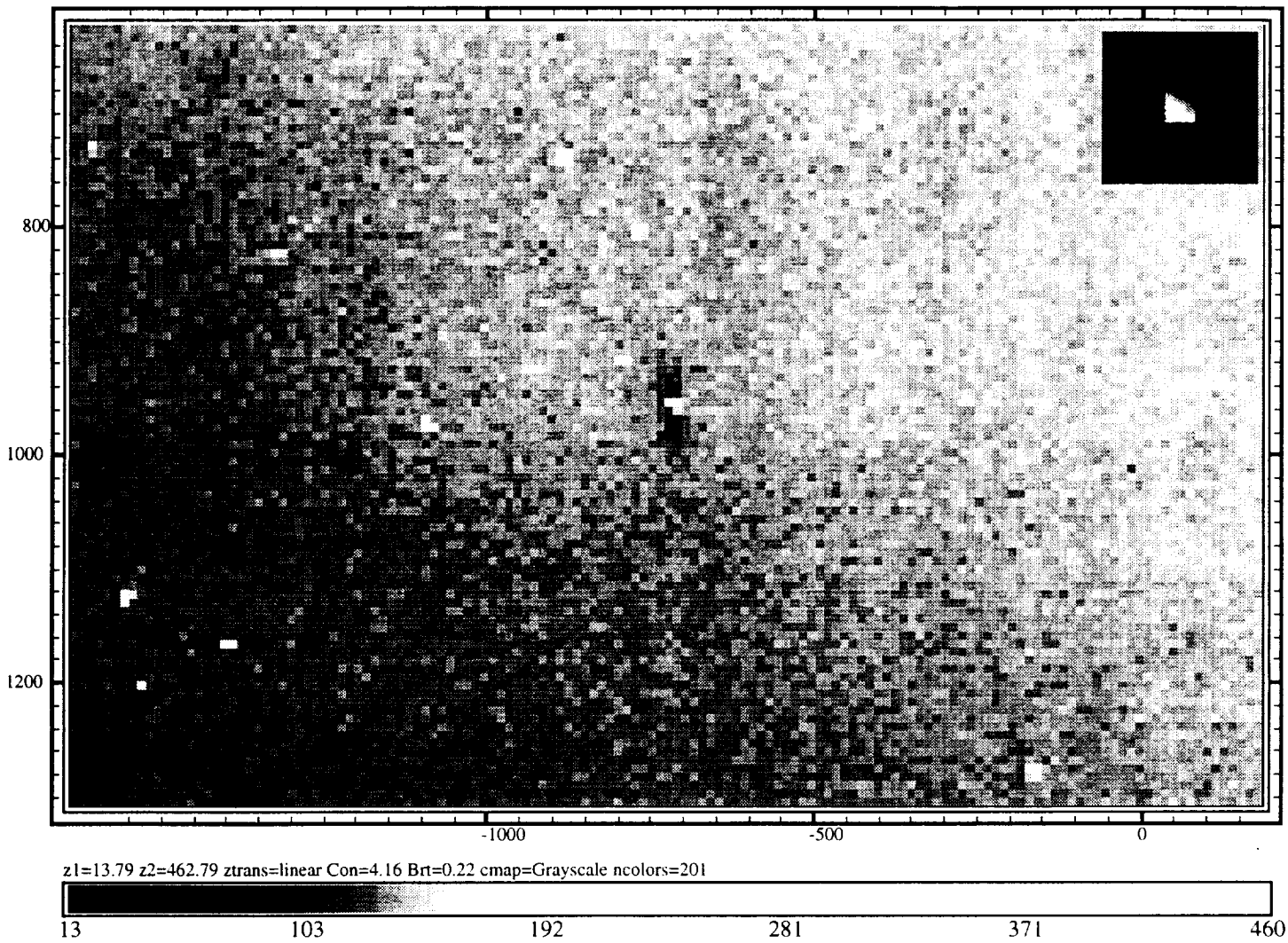

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