

DISSOCIATIVE RECOMBINATION OF MOLECULAR IONS WITH ELECTRONS

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Abstract

I will present an overview of the present state of the art of laboratory measurements of the dissociative recombination of molecular ions with electrons. Most work has focussed on obtaining rates and their temperature dependence, as these are of primary interest for model calculations of ionospheres. A comparison of data obtained using the microwave afterglow method, the flowing afterglow technique, and the merged beam technique shows that generally the agreement is quite good, but there are some serious discrepancies, especially in the case of H_3^+ recombination, that need to be resolved. Results of some earlier experimental work need to be reexamined in the light of more recent developments. I intend to point out such cases and will present a compilation of rate coefficients that have withstood scrutiny.

Recent advances in experimental methods, such as the use of laser-induced fluorescence, make it possible to identify some neutral products of dissociative recombination. I will briefly review what has been done so far and what results one might expect from future work.

Recombination rates and their dependence on temperature.

Traditionally, much of the experimental work on dissociative electron-ion recombination, i.e. a process of the type $AB^+ + e \rightarrow A + B$, has focussed on measurements of recombination rates and their dependence on electron temperature. Experimental techniques are either of the "swarm" type (microwave afterglow plasmas¹, flowing afterglow plasmas,² or shock tubes³) or they make use of single collision techniques (merged beams⁴ and ion traps⁵). In most cases, the agreement of results obtained by different methods is fairly good, as may be seen in Table I which contains a substantial subset of known recombination coefficients. The, historically oldest, microwave-afterglow technique, developed by Biondi¹, has contributed possibly the largest data base, but it has been discovered recently that the heating of electrons by application of microwave fields can be complicated in presence of molecular additives in the plasma afterglow⁶. The remarks entered in Table I point out cases where some revisions may be required. In several instances, the complications have been taken into account adequately (e.g. NO^+ , O_2^+) and the agreement among different methods is very good. A problem is likely to exist in the measurements of water and ammonia cluster ions. While no detailed calculations have been carried out, there is a strong suspicion that the observed lack of a variation of the recombination

coefficient with electron temperature was due to a strong reduction of the electron temperature resulting from inelastic collisions of electrons with water or ammonia molecules. The large 300 K values of α should be correct, however.

The history of the measurements of the H_3^+ recombination coefficient is rather complicated. A short time ago, it appeared to this author that the issue had been settled ⁷ and that the very small recombination rates found by the FALP technique ⁸ should be accepted, but new experimental data by Amano⁹ seem to suggest that the recombination rates are not as small as the FALP data. Theoretical calculations ¹⁰ clearly support the small values. In view of the importance of the H_3^+ ion, more experimental work is needed to resolve the problem.

Table I. Experimental data on electron-ion recombination coefficients $\alpha(T)$. Temperature exponent x defined by $\alpha(T) = \alpha(300\text{ K})(T/300)^{-x}$. Abbreviations of experimental methods: mwa-ms - microwave afterglow-mass spectrometer. mwa- microwave afterglow. MB=merged beam. FALP+ flowing-afterglow-Langmuir-probe. Trap-ion trap. Remarks. (A): no revisions required. (B): x is more likely to be about 0.5. (C): finding of $x=0$ may have been caused by lack of electron heating in the experiment. (D): Absolute value of a may be too high as a result of impurity ions in the afterglow. (E): α should be reduced by factor of two (Mitchell, private comm.). (F): Ions were vibrationally excited. (G): believed to refer to ions in $v=0$ vibr. state.

Ion	$\alpha(300\text{ K})$ [cm^3/s]	x	Temp. K	Method	Remarks	Ref.
NO^+	4.3 [-7]	0.38	300-4,600	mwa-ms		11
	4.2 [-7]	0.9	200-600	FALP		12
	2.3 [-7]	0.5	> 10,000	MB		13
	4.3 [-7]	0.85	300-5,000	trap		14
	4.4 [-7]	0.75	300-4,500	mwa-ms	(A)	15
N_2^+	1.8 [-7]	0.39	300-5,000	mwa-ms	(A)	16
	3.5 [-7]	0.5	300-10,000	MB	(E)	13
	2.2 [-7]	--	300	mwa-ms	(F)	17
	1.78 [-7]	0.37	700-200	shock tube		3

Table I continued

Ion	α (300 K) [cm ³ /s]	x	Temp. K	Method	Remarks	Ref.
O ₂ ⁺	1.95 [-7]	0.7	300-1200	mwa-ms	(A)	16
		0.56	1200-5,000	mwa-ms		
	1.95 [-7]	0.7	200-600	FALP		12
	1.95 [-7]	0.66	200-5,000	trap		14
	2.3 [-7]	0.5	300-10,000	MB		13
H ₃ ⁺	2.3 [-7]		300	mwa-ms	(D)	18
	1.7 [-7]	1.0	500-3000	mwa-ms	(D)	19
	~3.5 [-7]	0.5	0.01-0.7 eV	MB	(F)	20
	<2 [-8]	--	95, 300	FALP	(G)	12
	1.8 [-7]	--		afterglow		
HCO ⁺	2.0 [-7]	1	300, 205	mwa-ms	(A)	21
	1.1 [-7]	~0.8	300, 95	FALP		8
	2.4 [-7]	0.69	293- 5500	mwa-ms	(A)	22
H ₃ O ⁺ ·(H ₂ O)	2.5 [-6]	0.08	300-8000	mwa-ms	(C)	23
H ₃ O ⁺ ·(H ₂ O) ₂	3.0 [-6]	0.08	300-8000	mwa-ms	(C)	"
H ₃ O ⁺ ·(H ₂ O) ₃	3.6 [-6]	0	300-8000	mwa-ms	(C)	"
H ₃ O ⁺ ·(H ₂ O) ₄	~5 [-6]	0	300-8000	mwa-ms	(C)	"
H ₃ O ⁺ ·(H ₂ O) ₅	~5 [-6]	0	300-8000	mwa-ms	(C)	"
NH ₄ ⁺ ·(NH ₃)	2.82 [-6]	0.174	300-3000	mwa-ms	(C)	24
NH ₄ ⁺ ·(NH ₃) ₂	2.68 [-6]	0.05	300-3000	mwa-ms	(C)	"
NH ₄ ⁺ ·(NH ₃) ₃	~3 [-6]	0	200	mwa-ms	(C)	"
NH ₄ ⁺ ·(NH ₃) ₄	~3 [-6]	0	200	mwa-ms	(C)	"
N ₂ ⁺ N ₂	1.4 [-6]	0.41	300-6000	mwa-ms	(B)	25
CO ⁺ CO	1.3 [-6]	0.34	300-4000	mwa-ms	(B)	"
CO·(CO) ₂ ⁺	1.9 [-6]	~0	300-1000	mwa-ms	(B)	"
		0.33	1000-2000	mwa-ms	(B)	
O ₂ ⁺ O ₂	4.2 [-6]	0.48	143-5500	mwa-ms	(A)	26

Products of dissociative recombination

While the question of the rates of dissociative recombination can be regarded as reasonably well settled except for some important ions, the state of the art of determining the neutral products of dissociative recombination of polyatomic ions is far less well developed. Important progress has been made, especially by the Birmingham group who have developed laser-induced fluorescence techniques to quantitatively determine neutral products of dissociative recombination²⁷. The technique has been successfully applied to the ion HCO_2^+ . A similar experimental method, which also uses a flow tube, is presently being developed at the University of Pittsburgh. A related problem is that of determining the excited states of the neutral products of recombination of diatomic ions. Using vacuum uv absorption techniques, Rowe²⁸ has successfully detected metastable products of the recombination of N_2^+ and O_2^+ .

It appears likely that we will see considerable further progress in the area of measuring neutral products of recombination, but such work is far more difficult than measuring rate coefficients. In order to take advantage of these developments for planetary atmosphere modelling, it will be important to identify ions that are relevant to planetary atmospheres, and to establish cooperations between experimentalists and modelers.

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References

- 1 M.A. Biondi, in Applied Atomic Collision Physics, Vol. 3, Academic Press, New York 1982
- 2 D. Smith and N. G. Adams, in Physics of Ion-Ion and Electron-Ion Collision, F. Brouillard and J.W. McGowan eds., Plenum 1983
- 3 A.J. Cunningham and R.M. Hobson, J. Phys. B **5**, 2320 and 2328, (1972)
- 4 J.B.A. Mitchell, C.T. Ng, L. Forand, R. Janssen, and J.W. McGowan, J. Phys. B **17**, L909 (1984)
- 5 F.L. Walls and G.H. Dunn, J. Geophys. Res. **79**, 1911 (1974)
- 6 J.L. Dulaney, M.A. Biondi, and R. Johnsen, Phys. Rev. **A 34**, 3252 (1986)
- 7 See discussion by R. Johnsen, Int. J. of Mass Spectrometry and Ion Physics **81**, 67 (1987)
- 8 N.G. Adams, D. Smith, and E. Alge, J. Chem. Phys., **81**, 1778 (1984)
- 9 T. Amano, Ap. J. **329**, L121, (1988)

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- 10 H.H. Michels and R.J. Hobbs, *Ap. J. Lett.* **27**, L286(1984)
 - 11 C. Huang, M.A. Biondi, and R. Johnsen, *Phys. Rev. A* **11**, 901 (1977)
 - 12 E. Alge, N.G. Adams, and D. Smith, *J. Phys. B* **16**, 1433 (1983)
 - 13 P.M. Mui, and J.W. McGowan, *J. Phys. B*, **12** 1591 (1972)
 - 14 F.L. Walls and G.H. Dunn, *J. Geophys. Res.*, **79**, 1911 (1974)
 - 15 J.L. Dulaney, M.A. Biondi, and R. Johnsen, *Phys. Rev. A*, **36**, 1342 (1987)
 - 16 F.J. Mehr and M.A. Biondi, *Phys. Rev.* **181**, 264 (1969)
 - 17 E.C. Zipf, *Geophys. Res. Lett.* **4**, 661 (1980)
 - 18 M.T. Leu, M.A. Biondi, and R. Johnsen, *Phys. Rev. A*, **8**, 413 (1973)
 - 19 J.A. Macdonald, M.A. Biondi, and R. Johnsen, *Planet, Space Sci.* **32**, 651 (1984)
 - 20 J.B.A. Mitchell, C.T. Ng, L. Forand, R. Jannsen, and J.W. McGowan, *J. Phys. B*, **17** (1984)
 - 21 M.T. Leu, M.A. Biondi, and R. Johnsen, *Phys. Rev. A* **8**, 420 (1973)
 - 22 B. Ganguli, M.A. Biondi, R. Johnsen, and J.L. Dulaney, *Phys. Rev. A* **37**, 2543 (1988)
 - 23 C.M. Huang, M. Whitaker, M.A. Biondi, and R. Johnsen, *Phys. Rev. A* **18**, 64 (1978)
 - 24 C.M. Huang, , M.A. Biondi, and R. Johnsen, *Phys. Rev. A* **14**, 984 (1976)
 - 25 M. Whitaker, M.A. Biondi, and R. Johnsen, *Phys. Rev. A* **24**, 743 (1981)
 - 26 J.L. Dulaney, M.A. Biondi, and R. Johnsen, *Phys. Rev. A*, **37**, 2539 (1988)
 - 27 N.G. Adams, C.R. Herd, and D. Smith, *J. Chem. Phys.* **91**, 963 (1989)
 - 28 B.R. Rowe, in "Dissociative Recombination, Theory, Experiment and Applications", J.B. A. Mitchell and S.G. Guberman editors, World Scientific 1989