Optical emissions from the dissociative recombination of N$_2$H$^+$, HCO$^+$, HOC$^+$, and HNC$^+$

R Johnsen$^1$, M F Golde$^2$, R E Rosati$^3$, D Pappas$^4$, and M P Skrzypkowski$^5$

$^1$Department of Physics and Astronomy University of Pittsburgh, Pittsburgh, PA 15260, USA
$^2$Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA
$^3$Smithsonian Astrophysical Observatory, 60 Garden St. MS-50 Cambridge, MA, 02138, USA
$^4$Army Research Laboratory, 4600 Deer Creek Loop, Aberdeen Proving Ground, MD, USA
$^5$Prometheus Energy Company, 3311 S. 120th Place Suite 100, Seattle, WA 98168, USA

E-mail rj@pitt.edu

Abstract. We present recent flowing-afterglow measurements of branching fractions for electronically and vibrationally excited products arising from the dissociative recombination of N$_2$H$^+$, HCO$^+$, HOC$^+$, and HNC$^+$ ions with thermal electrons. State-specific yields were derived by fitting the observed, spatially resolved emission band intensities to models that simulate all ion-chemical processes, recombination, diffusion, and gas mixing.

1. Introduction

Absolute emission spectroscopy in recombining afterglow plasmas is currently the only method to determine branching fractions for radiating products of dissociative recombination (DR). This contribution summarizes the results of such measurements on the protonated species N$_2$H$^+$, HCO$^+$, HOC$^+$, and HNC$^+$ ions with thermal electrons. State-specific yields were derived by fitting the observed, spatially resolved emission band intensities to models that simulate all ion-chemical processes, recombination, diffusion, and gas mixing.

2. Experimental methods

Our flowing afterglow system consists of a small flow tube (diameter of 6 cm, length of 36 cm), equipped with a Langmuir probe to measure electron densities, two long spectroscopic windows, and a downstream quadrupole ion mass filter. The spectroscopic equipment, a movable monochromator/PMT system, covers wavelengths from 200 nm to 900 nm with bandwidths from 0.2 nm to 1.3 nm. Its spectral response was calibrated with deuterium and tungsten lamps. Almost all measurements were done in a spatially resolved fashion, i.e., emissions were recorded at several axial positions, and were compared to models that simulate the spatial/temporal evolution of the plasma. This procedure provides an essential consistency check of the kinetic models that are used in the data analysis. N$_2$H$^+$, HCO$^+$, HOC$^+$, and HNC$^+$ ions were derived via a sequence of ion-chemical steps from metastable helium atoms (He*) and a few He$^+$ ions that flow out of the microwave discharge in pure helium (see figure 1), followed by Penning ionization of argon gas, He* + Ar → He + Ar$^+$ + e$^-$. The initial upstream plasma contains mainly Ar$^+$ ions and electrons with number densities of typically 4 × 10$^{10}$ cm$^{-3}$. Subsequent reactions of Ar$^+$ with added N$_2$, H$_2$, CO, or HCN or suitable blends of those gases then produce the recombining luminous plasma (the “flame”).
Some metastable argon atoms (Ar*) enter the reaction zone and can give rise to background molecular emissions that have to be separated from those due to recombination; this can be done by adding an attaching gas (SF$_6$) that removes free electrons and thus eliminates DR. The total pressure in the flow tube in these experiments was on the order of 0.9 Torr (80% He, 20% Ar). The on-axis flow velocity of the buffer gases was typically $\approx 5900$ cm/s. The observable “flame” extends about 10 cm downstream from the reagent inlet, corresponding roughly to 2 ms of afterglow time.

3. Afterglow models

To derive product yields from the observed emission intensities, the concentrations of the recombining ions and electrons at each point in the afterglow plasma must be obtained by calculation. Our computer models simulate the diffusion of the reagents from the reagent inlet, transport of particles in the flow field, ambipolar diffusion of ions and electrons, destruction of active particles at the flow-tube walls, recombination, and radiation. The models generate the radial and axial density profiles of all relevant particles and predict the z-dependence of the recombination radiation (integrated over the radial coordinate along the line of sight of the monochromator) for trial yields of a particular electronic state. We insisted that the models adequately reproduce both the shape and the magnitude of the observed emissions for several reagent concentrations (see figure 2). To test the validity of the models, several experimental tests were made, and two independent computer models were developed. The first model uses an implicit-explicit algorithm for solving the coupled differential equations while the second uses simpler algorithms that can be implemented on a spreadsheet program and produces a graphical output in a time of a few seconds. Except for the short region a few millimeters downstream from the reagent inlet both models gave essentially identical results. The models also showed, somewhat surprisingly at first, that the volume emission rate of the recombination radiation downstream from the gas inlet has a minimum on the flow-tube axis. When a point-like gas inlet is used, the flame resembles a hollow rather than a solid cone. In the case of a ring-shaped inlet, a “windsock” might be a better descriptive term.
Figure 2: Example of computer fits (lines) to the measured axial dependence (data symbols) of an observed emission intensity. In the example, the CN($B–X$) intensities due to HNC$^+$ recombination were fitted for three HCN concentrations of $2.5\times10^{11}$ cm$^{-3}$ (diamonds), $3\times10^{12}$ cm$^{-3}$ (squares), and $5\times10^{12}$ cm$^{-3}$ (triangles). The HCN gas inlet was located at $z = 7$ cm. The only adjustable parameter in the fits was a single normalizing factor in the absolute intensity.

To determine absolute yields of for a particular electronic state, the axial ($z$) dependence of the intensity of all observable transitions from that state was compared to one of the CO bands arising from recombination of CO$_2^+$, for instance CO($a-X$), for which the yield has been determined previously [2] to be $0.29 \pm 0.10$. In practical work, to reduce errors due to possible drifts of the photometric detection efficiency, all intensity measurements were preceded and followed by reference measurements in recombining CO$_2^+$ afterglows.

4. Measurements and results

4.1 Emissions from $N_2H^+$ recombination

The dissociative recombination $N_2H^+\rightarrow N_2 + H$ with thermal electrons releases sufficient energy to populate N$_2$ in the ground state and in the following electronically excited states:

\[ N_2H^+ + e^- \rightarrow N_2(X^1\Sigma_g^+) + H(^3S) + 8.49\text{eV} \]
\[ \rightarrow N_2(A^3\Sigma_u^+) + H(^3S) + 2.32\text{eV} \]
\[ \rightarrow N_2(B^3\Pi_u) + H(^3S) + 1.14\text{eV} \]
\[ \rightarrow N_2(W^3\Delta_u) + H(^3S) + 1.13\text{eV} \]
\[ \rightarrow N_2(B'^3\Sigma_u^+) + H(^3S) + 0.33\text{eV} \]
\[ \rightarrow N_2(a'^3\Sigma_u^+) + H(^3S) + 0.09\text{eV} \]
Accessible vibrational states are: $A^3\Sigma^+_u\ (v \leq 15)$, $B^3\Pi_g\ (v \leq 5)$, $W^3\Delta_u\ (v \leq 6)$, $B'^3\Sigma^-_u\ (v \leq 2)$, and $a'1\Sigma^-_u\ (v = 0)$. Afterglow measurements of the total H-atom yield [6] have shown that dissociation into N$_2$ and H is the only important product channel. An earlier, disagreeing ion-storage ring measurement [7] has been traced to an error and has been retracted. As is discussed by Adams [8], new measurements again show that the H-atom yield is close to unity. The total recombination coefficient of N$_2$H$^+$ at 300 K (2.4×10$^{-7}$ cm$^3$/s) [9] is typical for a simple triatomic ion.

The principal kinetic processes in the N$_2$H$^+$ experiments, in which H$_2$ and N$_2$ were the molecular reagents, consist of the following fast ion-molecule reactions, followed by DR and radiation:

Ion formation:

$$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \quad \text{ArH}^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{Ar} \quad \text{H}_2^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}_2$$

Recombination: $\text{N}_2\text{H}^+ + e^- \rightarrow \text{N}_2(X, A, B, W, B') + \text{H}$

Radiation: $\text{N}_2 (B^3\Pi_g) \rightarrow \text{N}_2 (A^3\Sigma^+_u) + h\nu$

The H$_2$ concentrations were 4.16×10$^{12}$ cm$^{-3}$ and 1.22×10$^{13}$ cm$^{-3}$ while the N$_2$ concentrations were 3.66×10$^{13}$ cm$^{-3}$ and 1.17×10$^{14}$ cm$^{-3}$. All combinations of these concentrations were used.

In an earlier afterglow experiment, Adams and Babcock [10,11] observed strong N$_2 (B^3\Pi_g - A^3\Sigma^-_u)(v', v''\prime)$ emission in a recombining N$_2$H$^+/e^-$ afterglow plasma. Emission from $v' > 5$ was seen and ascribed to recombination of vibrationally excited N$_2$H$^+$, while the more relaxed vibrational distribution obtained at a higher N$_2$ concentration was thought to arise from N$_2$-induced vibrational relaxation of the N$_2$H$^+$ precursor.

Our analysis of the $B-A$ spectra showed that the vibrational distribution of the $B$-state shifted to lower states in the later afterglow. The effect depended only very weakly on the experimental H$_2$ and N$_2$ concentrations.
Vibrational relaxation of the recombining N$_2$H$^+$ in collisions with N$_2$ was invoked by Adams and Babcock, who observed a similar effect. However, since we did not find any significant changes when the concentrations of H$_2$ and N$_2$ were varied, we suggest as a second, perhaps more important mechanism, namely that recombination of N$_2$H$^+$ also produces N$_2$ in the nearby long-lived $W$-state and that collisionally induced and radiative transitions from $W$ to $B$ populate N$_2(B)$ in low vibrational states. This fits well with recent theoretical work by Talbi [12,13], who finds that dissociation into the $W$-state should be the dominant dissociation path in linear geometry. In a more realistic bent geometry, both the $B$ and $W$ states would be formed.

Using the absolute branching fraction for CO($d$) obtained in our previous work [1,2], we derived an effective spectroscopic yield for formation of N$_2(B)$ of 0.19±0.08. The combined yield of all triplet states ($B^3\Pi_u, B^3\Sigma_u^+, A^3\Sigma_u^+, W^3\Delta_u$) of N$_2$ could be significantly larger.

**4.2 Emissions from HCO$^+$, HOC$^+$ recombination**

Analyzing the recombination spectra emitted by the recombining formyl ion HCO$^+$ and its isomer HOC$^+$ presented a more challenging task than that encountered in the studies of N$_2$H$^+$. Recombination of HCO$^+$ and HOC$^+$ share the following three CO-forming branches, namely

$$\begin{align*}
\text{HCO}^+ + e^- & \rightarrow \text{CO}(X^1\Sigma^+) + \text{H}(^2\text{S}) + 7.31\text{eV} \\
& \rightarrow \text{CO}(a^3\Pi_g) + \text{H}(^2\text{S}) + 1.30\text{eV} \\
& \rightarrow \text{CO}(e^3\Sigma^-) + \text{H}(^2\text{S}) + 0.44\text{eV} 
\end{align*}$$

(3)

but HOC$^+$ (1.74 eV above HCO$^+$) recombination can form three additional states:

$$\begin{align*}
\text{HOC}^+ + e^- & \rightarrow \text{CO}(d^3\Delta_u) + \text{H}(^2\text{S}) + 1.53\text{eV} \\
& \rightarrow \text{CO}(e^3\Sigma^-) + \text{H}(^2\text{S}) + 1.29\text{eV} \\
& \rightarrow \text{CO}(A^1\Pi) + \text{H}(^2\text{S}) + 1.02\text{eV} 
\end{align*}$$

(4)

Recombination of HCO$^+$ in the vibrational ground state with 300 K electrons provides sufficient energy to populate the following vibrational levels of electronically excited states of CO: $a'(\nu' < 8)$, and $a'(\nu' < 4)$. Recombination of HOC$^+$ ions may populate $a(\nu' < 16)$, $a'(\nu' < 18)$, $d(\nu' < 13)$, and $e(\nu' < 11)$.

Extensive laboratory measurements [14,15,16,17,18,19,20,21,22] have shown that the recombination rate of HCO$^+$ with 300 K electrons is on the order of $2 \times 10^{-7}$ cm$^3$s$^{-1}$. However, theoretical calculations [23,24,25,26] so far have not reproduced this value and the question if HCO$^+$ recombines by a direct or indirect process has not been entirely resolved. The H-atom yield is known to be near unity [6,21]. Observations by Adams and Babcock [10] and Butler et al.[27] of CO($a^3\Pi - X^1\Sigma$) band emissions from recombining HCO$^+$ afterglows have shown that a fraction of CO is formed in the long-lived $a^3\Pi$ state.

Our experimental procedures were similar to those used in the N$_2$H$^+$ work, but the molecular reagents were H$_2$ and CO. Most of the kinetic processes that convert the initial Ar$^+$ ions to HCO$^+$ and HOC$^+$ in reactions with H$_2$ and CO are quite well known, with the unfortunate exception of some steps that determine the relative abundance of the two isomers. However, since the abundance of HOC$^+$ always remains at the level of only a few % of that of HCO$^+$, the uncertainty in the HOC$^+$ abundance has a fairly small effect on the determination of product yields of HCO$^+$, but a larger effect on the yields of HOC$^+$ recombination. Here, we have to omit the rather lengthy discussion of the ion chemistry that is described in more detail in the paper by Rosati et al. [4].

The observed emission spectra consisted of the ultraviolet CO($a - X$) bands and the visible/near infrared CO($a' - a$), CO($d - a$) and CO($e - a$) band systems. CO($a$) can be formed by recombination
of both isomers, but all levels $v' \geq 5$ of CO($a'$) and all levels of CO($d$) and CO($e$) must be ascribed to recombination of the HOC$^+$ since the upper levels are not energetically accessible to recombination of HCO$^-$. We do not observe that vibrationally excited HCO$^-$ was a significant source of the emissions that we ascribe to HOC$^+$, since we found no evidence for vibrational quenching of HCO$^-(v>0)$ with any of the added gases. Formation of CO($a', v' = 4$) from HCO$^-$ is close to thermoneutral and this state may be formed by both HCO$^-$ and HOC$^+$.

4.2.1 Formation of CO($a$) in recombination of HCO$^-$. At low concentrations of CO ($1 \times 10^{13}$ cm$^{-3}$), the vibrational distribution for levels $v = 0$ to 4 of CO($a$) was found to be $0.45 \pm 0.01, 0.21 \pm 0.01, 0.13 \pm 0.01, 0.10 \pm 0.01, 0.10 \pm 0.01$. Very weak emission from $v = 5$ was also detected. Further downstream the distribution shifted slowly towards lower vibrational levels, consistent with electronic quenching of the long-lived CO($a, v'$) by CO. The observed vibrational distributions for this state are quite close to those found by Butler et al. [27]. Both distributions are slightly colder than those calculated by Tomashevsky et al [26].

The spectroscopic CO($a$) yield from HCO$^- + e^-$ recombination was found to be $0.26 \pm 0.12$, where the uncertainty reflects our assessment of a possible systematic uncertainty in the CO($a$) yield from CO$_2^+ + e^-$. Random errors were far smaller. We estimate that indirect formation of CO($a$) via radiative transitions from the CO($a', d, e$) states contributes about 10% to the raw spectroscopic yield. Hence, the direct CO($a$) recombination yield from HCO$^-$ recombination should be $0.23 \pm 0.12$.

4.2.2 Formation of CO($a', d, e$) in recombination of HOC$^+$. The relative vibrational distribution for levels $v' = 5$ to 8 of CO($a'$) was: $0.59 \pm 0.03; 0.22 \pm 0.03; 0.12 \pm 0.01; 0.07 \pm 0.01$. Close to the reagent inlet, the population of CO($a', v' = 4$) was about 80% of that of $v' = 5$. For CO($d, v' = 0$–5), the relative populations were: $0.21 \pm 0.10; 0.16 \pm 0.05; 0.17 \pm 0.02; 0.28 \pm 0.01; 0.12 \pm 0.01; 0.05 \pm 0.01$. The weaker emission between 380 and 500 nm could be ascribed mainly to CO($d = a, v' = 0, 1$) bands. Approximate analysis of the band intensity in this region showed a gradual decrease in population in CO($d$) from $v' = 5$ to $v' = 9$. The ratio of the total observed population in CO($a', v' = 4$) to that in CO($d, v' = 0–5$) close to the reagent inlet was $1.12 \pm 0.03$. The CO($e = a$) emission occurs in a congested region between 490 and 590 nm. The ($v' = 0$) bands for $v' = 2–5$ can be tentatively assigned, with the (3, 0) band being the strongest. Populations of CO($e, v' = 3$) and of CO($e, v' = 2–5$) are estimated to be respectively about 2% and 5% of the total population of the CO($a', d, e$) states.

To summarize the HOC$^+$ yields: HOC$^+$ seems to recombine largely into the higher triplet states $a'$, $d$, and $e$. The combined yield of the three states is large, probably larger than 0.4, of which 20% go into $a'$, 18% into $d$, and 2 to 4% into $e$.

4.3 Emissions from HNC$^+$ recombination
Recombination of HNC$^+$ with thermal electrons has the following CN producing branches:

\[
\begin{align*}
\text{HNC}^+ + e^- & \rightarrow \text{CN}(B^2\Sigma^+) + H & + & 3.82 \text{ eV} \\
& \rightarrow \text{CN}(A^2\Pi) + H & + & 5.89 \text{ eV} \\
& \rightarrow \text{CN}(X^2\Sigma^+) + H & + & 7.02 \text{ eV}
\end{align*}
\]

The following vibrational states are energetically accessible: $B^2\Sigma^+ (v \leq 18), A^2\Pi (v \leq 34)$, and $X^2\Sigma^+ (v \leq 35)$. While most needed ion-molecule reactions involving HCN$^-$ and HNC$^+$ were known [28,29, 30,31,32], the rate and isomer branching of the Ar$^+$ + HCN $\rightarrow$ HCN$^+$ (HNC$^+$) + Ar reaction had to be measured by us in a separate drift tube experiment. By comparing the reactivities of the Ar$^+$ + HCN product ions with xenon we found that HNC$^+$, the lower-energy isomer, is by far the dominant product. Small amounts of HCN$^-$ may have been present in the afterglow measurements, but there was no positive indication of their presence. The recombination coefficient of HNC$^+$ of $2 \times 10^{-7}$ cm$^3$/s was obtained as part of this experiment, in good agreement with the result of a merged-beam measurement of Sheehan et al.[33].
Spectral scans of the emissions from the region downstream of the HCN inlet showed the well characterized [34] B-X violet bands as well as the A – X red bands of CN. Because of spectral congestion in some wavelength ranges, the analysis of the spectra was done, in part, by fitting them to synthetic spectra. In some measurements, xenon was added to destroy argon metastables that were found to produce some background emissions. Also, addition of hydrogen, which converts HNC+ ions to HCNH+, was found to strongly reduce all emissions, indicating that recombination of HCNH+ does not produce significant emissions.

4.3.1 B-state vibrational distribution. The form of the B – X violet recombination spectrum was essentially independent of HCN concentration and reaction time (with the exception of anomalous $v' = 11$) suggesting that the vibrational distribution of the recombining HNC+ ions is dominated by a single vibrational state, presumably the lowest state. Good fits by synthetic spectra required a rotational temperature of 2500 ± 500 K. For $v' = 0$ to 4, fairly reliable relative vibrational populations could be obtained which were 100: 58:6: 40:7: 25:5: 27:3. The relative populations of $v' = 5 – 10$ are less certain, but the fitting of the spectra suggested an average population per level of at least 25% of that of $v' = 0$. Emission from $v' = 11 – 15$ was too weak to allow useful comparisons with synthetic spectra, but the integrated emission intensity of these bands (between 390 and 410 nm) is one-half of the integrated intensity from $v' = 0 – 10$ (370 – 390nm), indicates very significant population of levels $v' = 11 – 15$. In summary, a very wide range of B-state vibrational levels, $v' = 0$ to 15 and beyond, is strongly populated in this reaction. The vibrational distribution is probably bimodal, with peaks at $v' = 0$ and at high $v'$. The lower levels are characterized also by a high rotational temperature.

4.3.2 A-state vibrational distribution. A-X spectra measured at different distances from the reactant inlet yielded consistent vibrational distributions. The relative populations of levels A, $v' = 2 – 15$ were: 11: 57: 80: 91: 91: 100: 80: 68: 45: 57: 41: 37: 34: 23, indicating an inverted distribution, peaking at levels $v' = 5 – 8$. We estimate that the derived populations of most levels have uncertainties of about 10%, but for the lowest and highest levels ($v' = 2 - 4$ and 12 – 15) the uncertainties are larger, about 30%. Unlike the CN(B) state, the radiative lifetime of CN(A) is sufficiently long (4 – 9 μs) so that rotational relaxation of CN(A) is expected to be complete.

4.3.3 B-state and A-state yields. The B-state yield, defined as the fraction of recombination events producing CN(B) in any of the observed vibrational states, was found to be 0.22±0.08, while the yield of CN(A) is somewhat smaller, namely 0.14±0.05. Since the B-A radiative transition probabilities are only of the order of 1% of those for B-X, radiative B-A transitions make a minute contribution to the observed CN(A) yield, much smaller than the quoted uncertainties, and have little effect on the vibrational distribution.

5. Conclusions

Afterglow emission spectroscopy, in conjunction with extensive model calculations, can provide fairly accurate absolute yields for radiating states formed by recombination. The experimental uncertainties in the absolute yields largely reflect the systematic uncertainty in the reference source intensity. The ratios of yields for different states of the same product are better determined. Hence, if later work shows that one of the measured yields is incorrect, all other yields would have to be corrected by the same factor. The spectroscopic yields of particular electronic states were found to be as large as ~ 20% of the total yield into all branches. Since usually not all optical transitions are observable, the true yields may be larger. We find that the vibrational distributions in some cases extend to high quantum numbers, and that they do not always follow a monotonic pattern. The observed vibrational distributions may contain valuable hints concerning dissociation mechanism. In some cases, vibrational excitation may come about because the equilibrium bond distance in the final state differs...
from that in the parent ion. It is also possible that some recombination processes proceed via long-lived complexes, in which case vibrational excitation could result from intramolecular energy transfer.

Rotational excitation of products was seen in only one case; nascent rotational excitation may be more common but is frequently not observable because rotational thermalization occurs before radiation.

We did not find clear evidence that the recombining ions had supra-thermal vibrational distributions. This should have been detectable by slow changes in the vibrational populations of the products, but was not seen. Perhaps, one should be more careful in invoking vibrational excitation to rationalize discrepancies in DR measurements. In one case (N$_2$(B) form N$_2$H$^+$), changes in vibrational product distributions were seen, but they were probably caused by mixing of the W and B states.

It is not possible at this time to compare our experimental findings to results of ab-initio theoretical calculations. Triatomic ions still pose a serious challenge to theory, and, although much progress has been made, there are no firm predictions of product branching yields of specified electronic and vibrational levels.

Acknowledgement: This work was, in part, supported by the NASA Planetary Atmospheres Program

References

[1] Rosati R E, Johnsen R and Golde M F 2003 J. Chem. Phys. 119 11630
[2] Skrzypkowski M P, Gougousi T, Johnsen R and Golde M F 1998 J. Chem. Phys. 108 8400
[3] Rosati R E, Johnsen R and Golde M F 2004 J. Chem. Phys. 120, 8025
[4] Rosati R E, Skrzypkowski M P, Johnsen R and Golde M F 2007 J. Chem. Phys. 126, 154302
[5] Rosati R E, Pappas D, Johnsen R and Golde M F J. Chem. Phys 2007 126, 154303
[6] Adams N G, Herd C R, Geoghegan M, Smith D, Canosa A, Gomet J C, Rowe B R, Queffelec J L, and Morlais M 1991 J. Chem. Phys. 94 4852
[7] Geppert W D, Thomas R, Semaniak J, Ehlerding A, Millar T J, Österdahl F, åf Uggglas M, Djuric N, Paal A and Larsson M 2004 Astrophysical J. 609 459
[8] Adams N G et al., this volume: New flowing afterglow technique for determining products of . . .
[9] Smith D and Spanel P 1993 Int. J. Mass Spectrom. Ion Processes 129 163
[10] Adams N G and Babcock L M 1994 J. Phys. Chem. 98 4564
[11] Adams N G and Babcock L M 1994 Astrophysical J. 434 184
[12] Talbi D 2007 Chemical Physics 332 298
[13] Talbi D et al., this volume: A comparative study of the DR reactions of c-C3H3+ and l- . . .
[14] Gougousi T, Golde M F and Johnsen R 1996 Chem. Phys. Lett. 265 399
[15] Lou M T, Biondi M A and Johnsen R, 1973 Phys. Rev. A 8 420
[16] Adams N G, Smith D and Alge E J 1984 Chem. Phys. 11 1778
[17] Ganguli B, Biondi M A and Johnsen R 1988 Phys. Rev. A 37 2543
[18] Amano T 1990 J. Chem. Phys. 92 6492
[19] Smith D and Spanel P 1993 Int. J. Mass Spectrom. Ion Proc. 129 163
[20] Le Padellec A, Sheehan C, Talbi, D and Mitchell J B A 1997 J. Phys. B 30 319
[21] Geppert W D, Thomas R, Ehlerding A, Hellberg F, Österdahl F, Millar T J, Semaniak J, Kaminska M, Källberg A, Paal A, Larsson M 2005, Journal of Physics Conference Series 4 26
[22] Rowe B R, Gomet J C, Canosa A and Mitchell J B A 1992 J. Chem. Phys. 96 1105
[23] Kraemer W P and Hazi A U 1998, in Dissociative Recombination: Theory, Experiment and Applications, edited by J.B.A. Mitchell and S.L. Guberman (World Scientific, Singapore 1998), p. 61
[24] Bates D R 1992, J. Phys. B 25 5479
[25] Larson A, Tonzani S, Santra R and Greene C H 2005 Journal of Physics Conference Series 4, 148
[26] Tomashevsky M, Herbst E and Kraemer W P 1998 Astrophysical J. 498 728
[27] Butler J M, Babcock L M and Adams N G 1997 Mol. Phys. 91 81
[28] Wisthaler A , Hansel A, Schwarzmann M, Scheirring Ch, Lindinger W and Ferguson E E 2000 J. Chem. Phys. 112 731
[29] McEwan M J 1992 , in “Advances in Ion Chemistry”, JAI Press 1992, Vol. J 24
[30] Petrie S, Freeman C G , McEwan M J and Ferguson E E 1991, Mon. Not. R. Astr. Soc. 248 272
[31] Hansel A, Glantschnig, M, Scheiring Ch, Lindinger W and Ferguson E E 1998 J. Chem. Phys. 109 1743
[32] Hansel A, Glantschnig, M, Scheiring Ch, Lindinger W and Ferguson E E 1998 J. Chem. Phys. 109 1748
[33] Sheehan C, Le Padellec A, Lennard W N, Talbi D and Mitchell J B A 1999 J. Phys. B 32, 3347
[34] Knowles P J, Werner, H-J, Hay P J and Cartwright D C 1988 J. Chem. Phys. 89 7334