Reliability of estimation of recombination energies of molecular radical cations by charge exchange and a test of the exoergicity rule

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Charge exchange occurring in a collision cell of a mass spectrometer was used previously to find the very long-lived excited electronic states of molecular cations generated by electron ionization. The underlying criterion in the method, called the exoergicity rule, was that only electronically exoergic and resonant processes have large cross sections at low collision energy. The validity of this rule has been checked in this work by estimating the recombination energies of some molecular ions based on the presence/absence of charge-exchange signals from gases with different ionization energies, and comparing these estimates with the literature values. It is concluded that a recombination energy can be estimated to within an upper limit uncertainty of 0.1 eV with this technique, which validates the exoergicity rule proposed previously. Copyright © 2003 John Wiley & Sons, Ltd.

Charge exchange is an important class of ion-molecule reactions. Charge exchange between atomic species has been heavily investigated over the years, both experimentally and theoretically.¹⁻⁴ The cross sections of atomic charge-exchange processes are known to be very sensitive to the absolute value of the change of internal energy (ΔE), for the reaction (1):

A⁺ + B → A + B⁺:

ΔE = IE(B) − RE(A⁺) (2)

Here, IE and RE denote the ionization and recombination energies, respectively, both of which are defined as positive quantities. For a resonant (ΔE = 0) charge exchange, the cross section is maximum at low collision energy and decreases rapidly as the collision energy increases. For endoergic (ΔE > 0) or exoergic (ΔE < 0) charge exchange, the cross section increases with the collision energy, reaches a maximum, then decreases at higher collision energy. The adiabatic maximum rule, which is a propensity rule based on the analysis of a large volume of experimental data, can predict the impact velocity (ν) at which the cross section is maximum with surprising accuracy⁵ as in Eqn (3). Use of 7 Å for the adiabatic parameter, a, has been reported to be adequate.

ΔE = a|ΔE|/h (3)

Charge exchange involving polyatomic species has been actively investigated also.⁶⁻¹¹ Here again, the cross section for a charge-exchange process which is highly endoergic (large positive ΔE) is generally small at low collision energy and increases with the collision energy. When a charge exchange is exoergic, on the other hand, energy resonance can be achieved for some vibrational levels of the products and a large cross section can be observed, unlike atomic cases. There have been many investigations of the mechanism of charge exchange, long-range vs. short-range, for example, and the importance of factors such as energy resonance, Frank-Condon factors for the process involved, etc. The general consensus seems to be that favorable Frank-Condon factors are not as important as initially thought for long-range charge exchange, which generally has a large cross section.¹¹⁻¹⁴ There is agreement on the importance of energy resonance, which can be easily achieved for electronically exoergic charge exchange involving complex molecules. This implies that exoergic charge exchange involving polyatomic species could occur efficiently under near thermal conditions, as manifested by strong signals generated in the ion source in conventional charge-exchange chemical ionization mass spectrometry.

When all the transitions from an excited electronic state of a polyatomic cation to lower-lying states are optically forbidden or have very small oscillator strengths, it is difficult to investigate such a state by spectroscopic means. Information on its energy relative to the ionic ground state can be obtained by photoelectron spectroscopy if the state is formed by removal of an electron from one of the occupied orbitals of the corresponding neutral. It is not possible, however, to judge from a photoelectron spectrum whether the excited electron...
state of interest would have a very long lifetime (1 μs or longer) because of rather poor resolution inherent in the technique. In fact, spectroscopic resolution required for such a judgment, $10^{-5}$ cm$^{-1}$ or better, exceeds the resolution of the state-of-the-art zero electron kinetic energy spectroscopy by orders of magnitude.

In our previous studies a charge-exchange technique was used to find cation states of benzene and its derivatives using the implicit assumption of the exoergicity criterion. To avoid confusion due to various ion-molecule reactions that may occur in high-pressure ion sources, charge exchange occurring in a separate cell was monitored. Molecular ions ($A^+$) generated in the source by electron ionization were decelerated and introduced to the cell containing a charge-exchange gas ($B$), and the ions generated from $B$ by charge exchange, such as $B^+$, were measured. When hardly any $B^+$ ions were observed, the charge exchange was assumed to be endoergic, while a prominent $B^+$ signal was taken as evidence for an exoergic process. By repeating the experiment with various charge-exchange gases with different ionization energies, the presence of molecular ions in electronic states above the ground state was sought. Since the long-lived excited electronic states found were well separated from others in energy, these states could be identified through such simple experiments.

It is thought that a more rigorous test is needed to check the capability of this technique as a method for accurate measurement of recombination energy [$RE(A^+)$] and for positive identification of the electronic state involved. This is all the more necessary because of the possible complications arising from the use of higher than thermal collision energy required in actual beam-gas experiments, and from the effects of vibrational energy of $A^+$ acquired at the time of electron ionization. Molecular ions of fluorobenzene, toluene, and chlorobenzene have been chosen here to test the accuracy of the recombination energies estimated by charge exchange, and thus the validity of the exoergicity rule. The first two ions named above, generated by electron ionization, were found to be in the ground electronic state only, while some of the third ion were found to be in an excited electronic state in our previous work. The results from the investigation are presented in this paper.

**EXPERIMENTAL**

A schematic diagram of the double-focusing mass spectrometer with reversed geometry, a VG ZAB-E (Micromass, Manchester, UK), modified for the present charge-exchange study, is shown in Fig. 1. Details of the experimental method have been described previously. Briefly, sample $A$ was introduced into the ion source at 140°C via a glass capillary connected to a reservoir (‘septum inlet’) and ionized by electron ionization using 16 eV electron energy. At this electron energy almost no fragment ions with large recombination energy, which can interfere with the present measurement, were produced. Ions were accelerated through a high voltage ($V_S$) of 4 kV. Reagent gas $B$ for charge exchange was introduced into the collision cell (see the inset of Fig. 1) located between the ion source and the magnetic sector, at a pressure corresponding to ~20% attenuation of the precursor ion beam. The collision cell was floated at high voltage ($V_C$) such that the precursor ion entering the cell had 50–500 eV translational energy. Ions exiting the collision cell, including those generated from the charge-exchange gas, were analyzed by scanning the magnetic sector as explained below. Measurements of ion kinetic energy with the electric sector were also made for positive identification of ions originating from the charge-exchange gas.

1,3-Butadiene and ethane were purchased from Matheson (Parsippany, NJ, USA). Other chemicals were purchased from Aldrich (Milwaukee, WI, USA). All chemicals were of the highest purity commercially available and were used without further purification.

**RESULTS AND DISCUSSION**

As described previously, three types (I, II, and III) of ions appear in the mass spectrum obtained by scanning the magnetic sector with charge-exchange gas in the collision cell floated at high voltage ($V_C$). These are ions generated in the ion source (type I), their collision-induced dissociation products (type II) generated in the collision cell, and ions originating from the gas in the collision cell (type III) generated by charge exchange. Taking $V_S$ as the acceleration voltage...
success or failure to observe charge-exchange signals for each precursor ion/charge-exchange gas pair is also shown in the table, which will be discussed below.

Figure 2(a) shows the mass spectrum of fluorobenzene recorded under the single-focusing condition measured with cis-2-butene (C₄H₈) in the collision cell. The acceleration voltage in the ion source was 4004 V and the collision cell was floated at 3958 V. Thus, the translational energy of C₆H₅F⁺ inside the cell (the collision energy) was 46 eV. Two type III peaks appear in the spectrum, at m/z 55.4 and 40.5. The fact that these were indeed type III peaks was confirmed by ion kinetic energy measurements with the electric sector, and also by changing the cell potential and tracking the peak positions using Eqns (6) and (7). The correct m/z values of these peaks, evaluated with these equations, are 56.0 and 41.0, corresponding to those of C₆H₅⁺ and C₃H₅⁺, respectively. C₃H₅⁺ could have been generated via dissociative charge exchange or via ion-molecule reactions of C₄H₈⁺ in the collision cell. Since C₆H₅F⁺ was in the ground electronic state, its recombination energy is equivalent to the first ionization energy of C₆H₅F, i.e. 9.2033 ± 0.0006 eV. Together with the ionization energy of 9.13 eV for C₃H₅, the charge exchange observed is exoergic by 0.07 eV. This appearance of strong charge-exchange signals at low energy collision (46 eV) is as expected from the exoergicity rule. We also evaluated the combined yield of C₆H₅⁺ and C₃H₅⁺ normalized to the precursor ion (C₆H₅F⁺) intensity measured in the absence of the charge-exchange gas. As shown in Fig. 3(a), the relative yield decreased with the collision energy. This is the same trend as observed for symmetric, or energy resonant, atomic charge-exchange reactions. Charge-exchange reactions with methylamine (CH₅N) and 1,3-butadiene (C₃H₅) both of which are electronically exoergic, displayed the same trend, as also shown in Fig. 3(a).

We attempted to measure charge-exchange signals using iodoethane (C₄H₈I), allene (C₃H₅), and vinyl bromide (C₂H₅Br). Calculated ΔV values for charge exchange of C₆H₅F⁺ with these molecules are 0.15, 0.46, and 0.60 eV, all endoergic. As shown in Fig. 3(a), the charge-exchange signals from these molecules were not observed at all at 46 eV

<table>
<thead>
<tr>
<th>Charge exchange gases</th>
<th>IE</th>
<th>Ref.</th>
<th>C₆H₅F⁺⁺</th>
<th>C₃H₅⁺⁺</th>
<th>C₄H₆Cl⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₆N (isopropylamine)</td>
<td>8.72 ± 0.03</td>
<td>21</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>CH₃N (methylamine)</td>
<td>8.9 ± 0.1</td>
<td>22</td>
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<td>O</td>
<td>O</td>
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<tr>
<td>C₃H₄ (cyclopentene)</td>
<td>9.01 ± 0.03</td>
<td>22</td>
<td>O</td>
<td>X</td>
<td>O</td>
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<tr>
<td>C₄H₆ (1,3-butadiene)</td>
<td>9.072 ± 0.007</td>
<td>22</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>C₅H₆ (cis-2-butene)</td>
<td>9.13</td>
<td>23</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>C₆H₈ (2-methyl-1-buten-3-yne)</td>
<td>9.25 ± 0.02</td>
<td>22</td>
<td>O</td>
<td>O</td>
<td>O</td>
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<tr>
<td>C₇H₈ (iodoethane)</td>
<td>9.3492</td>
<td>24</td>
<td>O</td>
<td>O</td>
<td>O</td>
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<tr>
<td>C₈H₈ (allene)</td>
<td>9.691 ± 0.004</td>
<td>25</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>C₉H₆Br (vinyl bromide)</td>
<td>9.804</td>
<td>26</td>
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<tr>
<td>CH₄Br (bromomethane)</td>
<td>10.54 ± 0.01</td>
<td>27</td>
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<tr>
<td>CH₃Cl (chloromethane)</td>
<td>11.28 ± 0.01</td>
<td>28</td>
<td>O</td>
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<td>O</td>
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<tr>
<td>C₂H₅ (acetylene)</td>
<td>11.4006</td>
<td>29</td>
<td>X</td>
<td>X</td>
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<tr>
<td>C₃H₇ (ethane)</td>
<td>11.521 ± 0.007</td>
<td>30</td>
<td>X</td>
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<td>X</td>
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<tr>
<td>Xe</td>
<td>12.12 ± 0.01</td>
<td>31</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

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collision energy. Thus, the cross sections for charge exchange with these molecules at 46 eV were smaller than those for exoergic cases by at least four orders of magnitude. Very weak charge-exchange signals were observed at higher collision energy, for example, at 200 eV for C₂H₅I. As mentioned above, the energy deficit in an electronically endoergic charge exchange may be overcome by use of the vibrational energy in the precursor ion or of the impact energy, i.e. the precursor ion translational energy. The fact that the former is not effective in this case is evident from the absence of charge-exchange signals for endoergic reactions at 46 eV. The weak signals at high collision energy indicate that conversion from the translational energy is somewhat effective, probably via short-range charge exchange.

Charge exchange of C₆H₅F⁺ with 2-methyl-1-buten-3-yne (C₅H₆, IE = 9.25 ± 0.02 eV) is an interesting case because ∆E = 0.05 ± 0.02 eV, i.e. only slightly endoergic. The reaction occurred efficiently, although the relative yield at 46 eV was noticeably lower than those for the electronically exoergic cases. Using the adiabatic maximum rule [Eqn (3)], we estimated the optimum energy transfer from the translational degree of freedom. This was 0.057 eV at the translational energy of 46 eV. Thus, even though charge exchange of C₆H₅F⁺ with C₅H₆ is endoergic by 0.05 ± 0.02 eV, as estimated from literature data, the reaction seems to occur efficiently aided by energy transfer from the translational degree of freedom. If the exoergicity rule is strictly applied, the recombination energy of C₆H₅F⁺ may be estimated as around 9.30 eV based on the results from studies with C₂H₅I and C₅H₆. This is larger than the correct value by 0.1 eV. When C₆H₅F⁺ in the ground electronic state undergoes recombination (neutralization) to an excited electronic state of the neutral, the recombination energy involved will be smaller than the ionization of C₆H₅F in the ground state. Such a possibility does not have to be considered here because the process involved would be much more endoergic than recombination to the ground state neutral.

According to our previous study, the toluene molecular ion C₇H₈⁺ generated by electron ionization undergoes rapid internal conversion to the ground electronic state, which has a
recombination energy of 8.8276 eV. Charge exchange of C$_2$H$_5^+$ with isopropylamine (C$_3$H$_7$N, IE = 8.72 ± 0.03 eV) is electronically exoergic by 0.11 ± 0.03 eV. Strong charge-exchange signals of C$_3$H$_7$N$^+$, C$_3$H$_8$N$^+$, and C$_3$H$_8$N$^+$ appear in the mass spectrum obtained at 46 eV collision energy (Fig. 2(b)), as expected from the exoergicity rule. Relative yields, measured as a function of the collision energy (Fig. 3(b)), show the same trend as for the exoergic charge-exchange reactions of C$_6$H$_5F^+$. Charge-exchange reactions of C$_6$H$_5^+$ with cyclopentene (C$_5$H$_8$) and 1,3-butadiene (C$_4$H$_6$) are endoergic with $\Delta E$ values of 0.182 ± 0.03 and 0.244 ± 0.007, respectively. Charge-exchange signals were not observed at all at 46 eV collision energy, as expected. Weak signals observed at 200 eV or higher collision energy (Fig. 3(b)) may be attributed to the participation of the impact collision energy as before. $\Delta E$ is 0.1 ± 0.1 eV for charge exchange with methylamine (CH$_3$N), i.e. either resonant or slightly endoergic. Strong charge-exchange signals were observed at 46 eV, with intensities which decreased with the collision energy. We cannot tell from these data alone whether the reaction is resonant or slightly endoergic.

Finally, similar experiments were performed for the chlorobenzene radical cation (C$_6$H$_5$Cl$^+$) generated by electron ionization. In our previous study$^{16}$ some of these ions were observed to remain in the B excited electronic state for a prolonged period (30 µs or longer). A study using C$_6$H$_5$Cl$^+$ is especially important because the exoergicity rule forms the basis for the method to find molecular cations in long-lived excited electronic states by charge exchange. A mass spectrum of C$_6$H$_5$Cl obtained at 46 eV collision energy, with CH$_3$Br (IE = 10.54 ± 0.01 eV) in the charge-exchange cell (Fig. 2(c)), shows prominent charge-exchange signals of CH$_3$Br$^+$ and CH$_3$Br$^+$. For reactions involving C$_6$H$_5$Cl$^+$ in the X (ground, RE = 9.0728 ± 0.0006 eV), A (RE = 9.707 eV), and B (RE = 11.3327 ± 0.0006 eV) electronic states, $\Delta E$ values are 1.47 ± 0.01, 0.83 ± 0.01, and −0.79 ± 0.01 eV, respectively. Efficient charge exchange with CH$_3$Br confirms the presence of C$_6$H$_5$Cl$^{+}$ in the B or higher excited electronic states. CH$_3$Cl (IE = 11.28 ± 0.01 eV) and other charge-exchange gases, for which exoergic charge exchange is possible with C$_6$H$_5$Cl$^{+}$ in the B state, also generated strong charge-exchange signals. As the collision energy was increased, relative yields of charge exchange with these gases decreased (Fig. 3(c)), indicating the resonant nature of the charge-exchange processes involved. With C$_7$H$_8$ (IE = 11.4006 eV), C$_8$H$_8$ (IE = 11.521 ± 0.007 eV), and Xe (IE = 12.12 ± 0.01 eV), charge exchange of C$_6$H$_5$Cl$^{+}$ in the B state becomes endoergic with $\Delta E = 0.0674 ± 0.0006, 0.188 ± 0.008$, and $0.79±0.01$ eV, respectively. None of these gases produced measurable charge-exchange signals at 46 eV collision energy, while very small signals become observable at higher collision energy (Fig. 3(c)). These data are entirely compatible with our previous proposition$^{15}$ that the B state of C$_6$H$_5$Cl$^{+}$ is very long-lived. From the perspective of the present study, it is important to note that the charge exchange with CH$_3$H$_2$ which is endoergic by only 0.0674 ± 0.0006 eV, is not detectable at 46 eV collision energy. From the charge-exchange data with CH$_3$Cl and C$_2$H$_2$, a recombination energy of around 11.34 eV may be estimated for the electronic state of C$_6$H$_5$Cl$^{+}$ involved in the reaction. This is higher than the correct value for the B state by 0.01 eV.

To summarize, the recombination energies of molecular cations estimated by charge exchange with various gases are in surprising agreement with the ionization energies relevant to the electronic states involved. A limitation of this technique is that measurements cannot be made with nearly continuous variation of $\Delta E$. Possible inaccuracy of ionization data available for charge-exchange gases is another limitation. By accepting the ionization energy data in the literature, and provided that charge-exchange gases with any ionization energy values as needed are available, the recombination energy estimated with this method is likely to be accurate to within 0.1 eV. Alternatively, the correct value may be lower only by 0.1 eV than that estimated by observing presence/absence of charge-exchange signals at low collision energy. The upper limit of 0.1 eV uncertainty is set here to accommodate the possible effects of conversion of the center-of-mass collision energy to the internal energy.

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**Figure 3.** Relative yields of the ions generated from a charge-exchange gas versus the precursor ion translational energy. Precursor ions are (a) C$_6$H$_5F^+$, (b) C$_7$H$_6^+$, and (c) C$_8$H$_6Cl^+$.
Finally, it is interesting to note that substantial vibrational energies in the molecular ions generated by electron ionization are not effective to help overcome endoergicities, especially for cases with slightly positive $\Delta E$. A plausible explanation is as follows. Since molecular ions with large internal energy disassociate rapidly in the ion source, molecular ions exiting the source would have internal energy less than or a little larger than the critical energy for the least endoergic dissociation channel. Let us suppose that a molecular cation consisting of 12 atoms (30 vibrational modes) possesses as much as 3 eV internal energy. Assuming equipartitioning of this energy, energy in each mode would be 0.1 eV only. That is, each vibrational mode would be mostly in the ground or low excited vibrational states. Then, only a very small fraction of the total internal energy can be released in the recombination process if it is assumed that multiple mode interactions are not possible under these conditions.

CONCLUSIONS

Neither exoergic nor endoergic reactions have a large cross section for atomic charge exchange at low collision energy. The same is true for endoergic ($\Delta E > 0.1$ eV) charge exchange involving polyatomic species. On the other hand, the cross section for an exoergic charge exchange is substantial, or maximum, at low collision energy for molecular cases. Also, the cross section for an exoergic charge exchange decreases with the collision energy, indicating dominance of energy resonant processes. Participation of vibronically energy resonant processes must be responsible for such observations. This phenomenon was called the exoergicity rule in our previous work,15,16 and utilized to find the presence of long-lived excited electronic states of molecular cations generated by electron ionization. The validity of this rule has been tested in the present work by estimating the recombination energies of molecular ions based on the presence/absence of charge-exchange signals from gases with different ionization energies. The recombination energies thus estimated were equivalent to or larger than the literature data by only 0.1 eV, which validates the exoergicity rule.

For an excited electronic state to have a very long lifetime, one of the requirements is that all the transitions from this state to lower-lying electronic states be optically forbidden or have very small oscillator strengths. Then, it becomes extremely difficult to probe the presence of such a state by spectroscopic means. With the exoergicity rule well established in this work, the charge-exchange technique is a powerful tool to detect the presence and identify the nature of the long-lived excited electronic states of polyatomic cations in such cases.

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REFERENCES


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