Mechanism of Energy Transfer in Collisional Activation of Kiloelectron-Volt Macromolecular Ions

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An impulsive collision theory explains why helium is an effective target gas for collisionally activated decomposition of large biological ions.

Knowledge of mechanisms of collisional energy transfer is fundamental to many areas of chemistry and physics. During recent years, it has become possible to produce beams of molecule-ions with masses above 20,000 u [1–4]. This has permitted a range of biological important compounds to be subjected to tandem mass spectrometry (also known as mass spectrometry/mass spectrometry), one of the most powerful of analytical methods [5–8]. With this method, the molecule-ion accelerated to about 10 keV is collided with a target gas. Excitation energy is taken up by the ion, and fragmentation is induced. The fragmentation provides structural information about the ion and hence about the neutral precursor.

Any gas may be used for collisional activation, but in practice He is commonly employed for activation of large organic and biological ions [5–8]. This is surprising when the maximum amount of energy available per collision for transfer to the internal degrees of freedom is considered. This quantity (the centre-of-mass) energy is given by

$$E_{\mathrm{cm}} = \frac{m_{\mathrm{g}}}{m_{\mathrm{i}} + m_{\mathrm{g}}} E_{\mathrm{i}} \,. \tag{1}$$

m_{g} and m_{i} are the masses of the target gas and the ion, respectively, and E_{i} is the initial translational energy of the ion. As is evident from (1), E_{cm} increases when m_{g} increases. The magnitude of E_{cm} is therefore not likely to be the only factor which determines the energy transfer to the ion. The important point is the efficiency of energy transfer, which can be formulated in the following way

$$Q = \varepsilon\, E_{\mathrm{cm}} \,. \tag{2}$$

Q is the energy uptake of the ion and ε is an efficiency factor. The approximately linear relationship between Q and E_{i} implied by (1) and (2) has support from recent experiments [9, 10].

Previous investigators have reported a correlation between the ionisation energy (IE) of the target gas and the amount of energy transferred to small- and medium-sized ions [11] and to macromolecular ions [5, 12]. On these grounds, it has been proposed that electronic excitation of the target gas determines the energy left for excitation of the ion. However, since mainly the noble gases have been investigated, this correlation may turn out to be apparent rather than real. Because the IE's of the noble gases decrease with increasing mass, it may very well be that the mass of the collision gas is the important factor for the efficiency of the energy transfer. Recently performed experiments support this assumption [9, 10]. When D_2 ($m_{\mathrm{g}} = 4$, IE = 15.5 eV) was used as collision gas, the energy transfer was the same as for He ($m_{\mathrm{g}} = 4$, IE = 22.5 eV), and both appeared to the more efficient than Ar ($m_{\mathrm{g}} = 40$, IE = 15.76 eV). In this note we outline a theory which a) accounts for mass dependency of energy transfer in collisions and b) can be used in order to quantitatively predict the energy transfer.

The interaction between ion and target is too fast (of the order 10^{-14} s for 10 keV and 1000 a.m.u.) for statistical distribution of E_{cm} in a collision complex to occur. It is therefore not unreasonable to assume that only momentum (and not potential energy) is transferred in a highly localised interaction. This approach has proved to be successful in predicting the energy transfer in high-temperature collisions between highly energized bromine and the noble gas [13]. Following Nordholm et al. [13], it can be shown that energy transfer in an impulse collision is given by

$$Q = \tfrac{1}{2} \chi\, E_{\mathrm{cm}} \,, \tag{3}$$

where

$$\chi = 4 \frac{m_{\mathrm{g}}\, m_{\mathrm{a}}}{(m_{\mathrm{g}} + m_{\mathrm{a}})^2} \,. \tag{4}$$

m_{a} is the mass of the atom of the ion which is hit by the target gas atom or molecule. In this version of the theory, E_{cm} is the only contribution to the kinetic energy available for transfer. In a more refined form, contributions from internal movement in the ion and thermal energy in the target gas should be added [13].

Because a large ion consists of several different atoms, a careful consideration is necessary in order to find a representative value of m_{a}. A value of 7.2 is used here for m_{a} as being representative of a typical peptide, on the basis that there are not geometric factors favouring one type of atom over another. Were there to be a preference for interaction with H atoms due to these tending to be on the "outside" of a peptide ion, the average effective value of m_{a} should be lower. In Table 1,

Table 1. The relationship between the energy transfer efficiency factor and masses of the target gas m_{g} and the atom which "is hit" in the ion.

m_{a}	m_{g}	
	4 (He)	40 (Ar)
1 (H)	0.32	0.05
7.2 (average in peptides)	0.46	0.26
12 (C)	0.38	0.35

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calculated mass dependencies of the efficiency are demonstrated. It can be seen that the closer is the match between the masses of the two atoms involved, the more efficient is the transfer.

It is not possible at the present time to find accurate experimental data on Q in order to evaluate our calculated values. The reason for this is the many difficulties associated with such an experiment. A careful consideration of the ion optics of the instrument and a better knowledge of the energy transfer as a function of the scattering angle is required. Work is in progress in this laboratory to overcome these problems and to explore further consequences of the theory presented here.

What is clear is that impulsive collisions would lead to greater proportions of the centre-of-mass collision energy being taken up by an organic ion when the target gas is He, as compared to Ar. Impulsive collisions would lead to more internal energy being taken up by an organic ion when the incident ion energy E_i is higher. We would suggest that simple impulsive interactions such as described here provide a good starting point for more detailed treatments of collisions between massive organic ions with kiloelectron volt translational energies and thermal gases.

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