



# An exact hard-spheres scattering model for the mobilities of polyatomic ions

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## Abstract

We describe an exact hard-spheres scattering model for calculating the gas phase mobilities of polyatomic ions. Ion mobility measurements have recently been used to deduce structural information for clusters and biomolecules in the gas phase. In virtually all of the previous ion mobility studies, mobilities were evaluated for comparison with the experimental data using a projection approximation. Comparison of the collision integrals calculated using the exact hard-spheres scattering model with those estimated using the projection approximation shows that large deviations, over 20%, occur for some geometries with grossly concave surfaces.

The mobility of a polyatomic ion depends on its structure [1–3]. Ion mobility measurements can resolve structural isomers and provide information about their geometries. This technique has been particularly valuable in the study of medium-sized clusters where spectroscopic information is difficult to obtain [4–10]. For example, chains, a variety of ring isomers, graphite sheets, and fullerenes have been observed for carbon clusters [7–10]. Recently, this approach has also been used to examine the conformations of peptides [11] and proteins [12] in the gas phase. Furthermore, instrumental advances now make it possible to perform high-resolution ion mobility measurements where isomers with very similar geometries can be resolved, as demonstrated by some recent studies of  $(\text{NaCl})_n\text{Cl}^-$  clusters [13]. Information about the geometries is obtained by comparing

measured mobilities with mobilities calculated for an assumed geometry. The zero-field mobility can be obtained from [14]

$$K = \frac{(18\pi)^{1/2}}{16} \left[ \frac{1}{m} + \frac{1}{m_b} \right]^{1/2} \frac{ze}{(k_B T)^{1/2}} \frac{1}{\Omega_{\text{avg}}^{(1,1)}} \frac{1}{N}. \quad (1)$$

In this expression,  $m$  is the mass of the ion,  $m_b$  is the mass of a buffer gas atom,  $N$  is the buffer gas number density,  $T$  is the temperature,  $ze$  is the charge, and  $\Omega_{\text{avg}}^{(1,1)}$  is the orientationally averaged collision integral. The collision integral is related to the scattering angle, the angle between the trajectory before and after a collision between the ion and a buffer gas atom. The orientationally averaged collision integral is calculated by averaging the momen-

tum transfer cross section over the relative velocity and the collision geometry [15]:

$$\begin{aligned} \Omega_{\text{avg}}^{(1,1)} &= \frac{1}{4\pi^2} \int_0^{2\pi} d\theta \int_0^\pi d\varphi \sin\varphi \int_0^{2\pi} d\gamma \frac{\pi}{8} \\ &\times \left( \frac{\mu}{k_B T} \right)^3 \int_0^\infty dg e^{-\mu g^2 / 2k_B T} g^5 \\ &\times \int_0^\infty db 2b(1 - \cos\chi(\theta, \varphi, \gamma, g, b)). \end{aligned} \quad (2)$$

In this expression  $\theta$ ,  $\varphi$  and  $\gamma$  define the collision geometry,  $\chi(\theta, \varphi, \gamma, g, b)$  is the scattering angle,  $g$  is the relative velocity,  $\mu$  is the reduced mass, and  $b$  is the impact parameter<sup>1</sup>. For a collision between two hard spheres Eq. (2) reduces to  $\pi b_{\text{min}}^2$ , where  $b_{\text{min}}$  is the hard-sphere contact distance. For a polyatomic ion, the most rigorous approach to evaluate the collision integral is to propagate trajectories in a realistic potential to determine the scattering angle, while averaging over the variables in Eq. (2). Mesleh et al. [16] have recently employed this method to calculate mobilities for fullerenes using an effective potential consisting of a sum of two-body Lennard–Jones interactions and ion-induced dipole interactions. However, this approach is extremely computationally intensive even for small clusters with relatively symmetric geometries, and requires information about the intermolecular potential which is often not readily available. In all of the other previous work, the collision integral has been approximated by

$$\Omega_{\text{avg}}^{(1,1)} \approx \frac{1}{4\pi^2} \int_0^{2\pi} d\theta \int_0^\pi d\varphi \sin\varphi \int_0^{2\pi} d\gamma \pi b_{\text{min}}^2, \quad (3)$$

where  $b_{\text{min}}$  is the minimum impact parameter for a collision geometry defined by  $\theta$ ,  $\varphi$ , and  $\gamma$  that avoids a hard-sphere contact with any atom in the cluster. This approach was first employed by Jarrold

and Constant [17] to deduce information about the shapes of silicon clusters. They used simple shapes so that the integrals could be solved analytically. Von Helden et al. [7] generalized the model by replacing the cluster by a collection of hard spheres, one for each atom in the cluster, and performing the integrations numerically. This method has been widely adopted in the last few years [4–12,18–20].

While it is clear that Eq. (3) ignores the long-range interactions between the polyatomic ion and buffer gas atom, it is perhaps less obvious that it also ignores all the details of the scattering process and effectively replaces the collision integral by an orientationally averaged projection. In this contribution we examine the validity of this approximation. We will show that for any body with only convex surfaces, the exact orientationally averaged hard-spheres collision integral is equal to the orientationally averaged projection. However, for bodies with concave surfaces this is not true. We have developed a rigorous hard-spheres scattering model to determine the magnitude of the deviation. For some geometries the collision integral determined from the exact hard-spheres scattering model differs from the orientationally averaged projection by over 20%. Since agreement between measured and calculated mobilities of better than 2% is generally used as a criterion for assigning geometries in these studies [7], this clearly could lead to the wrong structural assignments!

For a collision between two hard spheres the collision integral,  $\Omega$ , is equal to the projection,  $P$  ( $\Omega = \int db 2b(1 - \cos\chi) = \pi b_{\text{min}}^2$ ). In the following we prove that this is true for all locally convex bodies. Consider a finite planar figure with an arbitrary shape and area  $S$ . When this figure is positioned in space such that the angle between the normal to its plane and the vector  $x$  is equal to some  $a$ ,  $\omega = 2S \cos^3 a$  and  $p = S \cos a$ , where  $\omega$  is the momentum transfer cross section and  $p$  is the projection along a specific direction. Integrating over all angles

$$\Omega = 2S \frac{\pi \int_0^{\pi/2} \cos^3 a \sin a da}{\int_0^{\pi/2} a da} = \frac{S}{2}, \quad (4)$$

$$P = S \frac{\pi \int_0^{\pi/2} \cos a \sin a da}{\int_0^{\pi/2} a da} = \frac{S}{2}, \quad (5)$$

<sup>1</sup>Note that the definition of the collision integral employed here differs from that given by Hirschfelder et al. [15]. Following Mason and McDaniel [14], a factor of  $(k_B T / 2\pi\mu)^{1/2}$  present in the definition of Hirschfelder et al. is incorporated into Eq. (1) rather than in the equation for the collision integral.

thus  $\Omega = P$ . Since any finite geometric surface can be considered as a set of infinitesimally small, flat differential elements, one can express its cross section (projection) as a sum of the cross sections (projections) of these elements, if and only if these elements do not interact. There are two mechanisms for interactions: mutual shadowing of elements from direct collisions and multiple collisions where an atom is reflected from one element to another. To exclude both these effects, the requirement that the surface be locally convex at each point is necessary and sufficient. Whenever a surface satisfies this requirement,  $\Omega = P$ .

While, strictly speaking, the above derivation does not prove that bodies with concave surfaces could not have  $\Omega = P$ , it strongly suggests that this equality does not hold for such bodies in general. To verify this, we have developed a computer code to find the true hard-sphere collision integral for an arbitrary body. This is accomplished by solving

$$\Omega_{\text{avg}}^{(1,1)} = \frac{1}{4\pi^2} \int_0^{2\pi} d\theta \int_0^\pi d\varphi \sin \varphi \int_0^{2\pi} d\gamma \times \int_0^\infty db \, 2b(1 - \cos \chi(\theta, \varphi, \gamma, b)) \quad (6)$$

numerically. The scattering angle,  $\chi$ , is determined by following the trajectory through any and all of its collisions with the cluster until it leaves the cluster for good. This accounts for multiple collisions where a trajectory is reflected from one part of the cluster onto another part. Since all polyatomic ions consist of discrete atoms, parts of their surfaces are technically concave. Consequently, the exact hard-sphere collision integrals of all polyatomic ions deviate from their projections. However, one would expect larger deviations to occur for structures that are also concave on a gross scale, such as rings and cups. To determine the magnitude of these deviations we have performed calculations for a range of carbon cluster geometries. Carbon clusters have been the object of intense investigation over the last decade, including extensive ion mobility studies of carbon cluster cations and anions. A wide variety of isomers have been observed: linear chains, planar monocyclic, bicyclic and polycyclic rings, graphite sheets, fullerenes, fullerene dimers, and fullerene clusters. The existence of cups [21] and three-dimensional rings [19,20] has also been suggested.

In order to calculate the exact hard-sphere collision integral and the projection it is necessary to define a value for the hard-sphere contact distance. This was done by fitting the measured 298 K mobility of fullerene  $C_{60}^+$ , treating the hard-sphere contact distance as an adjustable parameter. Fullerene  $C_{60}^+$  was selected because its geometry is experimentally known [22]. The hard-sphere contact distances obtained were 2.81 Å using the exact hard-spheres scattering model and 2.86 Å using the projection approximation. If the same hard-sphere contact distance is used with both models, then the collision integral obtained from the exact hard-spheres scattering model is larger than that estimated from the projection approximation, in all the cases we have examined. Calculations using these parameters have been performed for a range of carbon cluster geometries. The geometries used are as follows. Linear chains and rotationally symmetric monocyclic rings were constructed using an interatomic distance [23] of 1.30 Å. Bicyclic rings generated by a [2 + 2] cycloaddition and large ( $n > 90$ ,  $n$  is the number of atoms) tricyclic rings were optimized in plane using the strain minimization procedure of Shelimov et al. [10]. Geometries for small tricyclic rings (planar or nearly planar) were obtained from von Helden et al. [7] and Strout et al. [19]. Graphite sheets are MNDO-optimized geometries [24] up to  $n = 70$  and unoptimized hexagonal assemblies for larger sizes. The fullerene geometries employed were experimental [22] for  $n = 60$  and MNDO for  $n = 20$  and 34 (Shelimov [24]), 70 (Raghavachari [25]), 120 (Murry et al. [26]) and 180 (Bakowies et al. [27]). For  $n = 240$  and  $n = 540$  fullerenes, calculations were performed using the geometries obtained by both Bakowies et al. [27] using MNDO and by Scuseria [28] with ab initio Hartree–Fock.

Fig. 1 shows a plot of the quantity  $\Omega_{\text{REL}} = \Omega(2.81 \text{ \AA})/P(2.86 \text{ \AA}) - 1$  (relative deviation of the collision integral calculated using the exact hard-sphere scattering model from the orientationally averaged projection) against  $(\text{cluster size})^{1/3}$  for a variety of different carbon cluster geometries. The relative deviations range from  $-3\%$  to over  $+5\%$ . Note that significant deviations are observed for linear chains, graphite sheets and fullerenes even though these geometries do not have grossly concave surfaces. The deviations result from ‘surface roughness’ such

as the dips in the middle of hexagons. For these three geometries, the deviations become more positive with increasing cluster size. This is because, for all contiguous bodies, the average surface curvature decreases with increasing size provided that the shape is constant, and this curvature mitigates the effects of surface roughness by reducing the number of multiple collisions. Similarly, the fact that  $\Omega_{REL}$  is always smaller for fullerenes than for the graphite sheet isomers is due to the higher average curvature of fullerene surfaces. For all the ring isomers  $\Omega_{REL}$  shows a maximum. Space-filling models of small rings indicate that they do not really have holes, hence the number of multiple collisions is small. As the ring size increases, collisions in which the buffer gas atom bounces from one side of the ring to the other become important and  $\Omega_{REL}$  increases. As the ring becomes even larger, the probability of multiple collisions decreases and the deviations decrease. Note that the maximum  $\Omega_{REL}$  increases on moving from monocyclic to tricyclic rings, while the position of maximum shifts to larger cluster size.

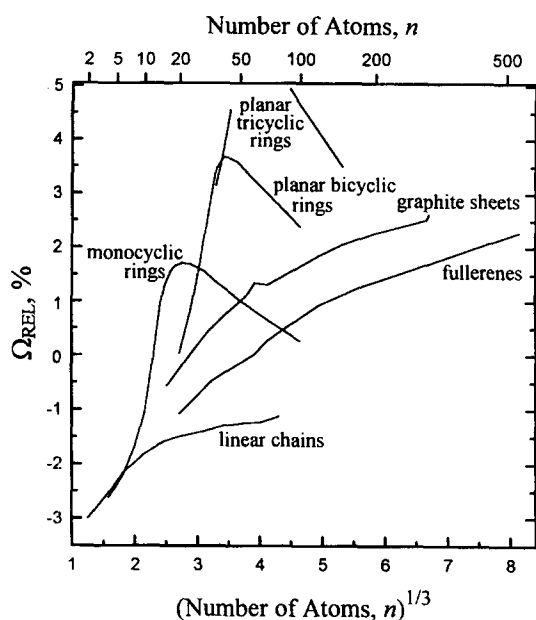


Fig. 1. Comparison of the collision integrals calculated using the exact hard-spheres scattering model with those estimated using the projection approximation. The figure shows a plot of the quantity  $\Omega(2.81 \text{ \AA})/P(2.86 \text{ \AA})-1$  against the  $(\text{number of atoms in the cluster})^{1/3}$  for a variety of different geometries (see text).

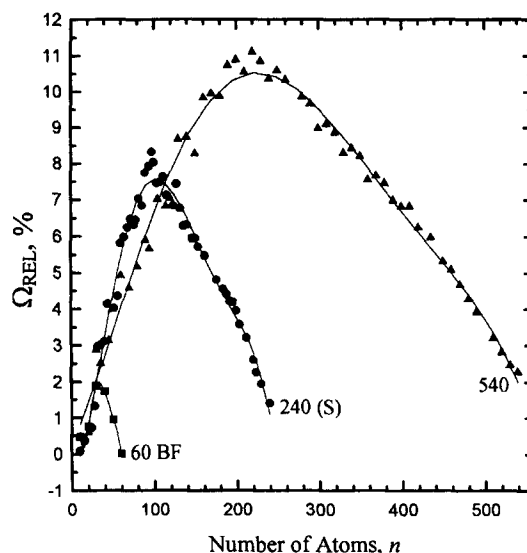


Fig. 2. Plot of the quantity  $\Omega(2.81 \text{ \AA})/P(2.86 \text{ \AA})-1$  against the number of atoms for cups derived from  $C_{60}$  (squares),  $C_{240}$  (S) (circles), and  $C_{540}$  (triangles) fullerenes, as described in the text. The fullerene geometries are from York et al. [36] for  $C_{240}$  and from Scuseria [28] for  $C_{540}$ . The lines are the fifth-order regressions through the points.

We now address a geometry with grossly concave surfaces: cups. Smalley [21] has suggested that cups, or open fullerenes, are transient intermediates in the gas-phase assembly of fullerene cages. Experimental studies have shown that fullerenes can be synthesized by the coalescence and subsequent annealing of carbon rings [29–31]. Furthermore, there are no features present in the ion mobility measurements in the region allocated for cups by the projection approximation [7]. The merits of the competing models for fullerene assembly have been the subject of a lively debate, as reflected in a recent review by Goroff [32]. Thus the accurate evaluation of the collision integrals for cups is of considerable importance. We have calculated collision integrals for a number of cups using the projection approximation and the exact hard-spheres scattering model. The cups were constructed by cutting a fullerene by a plane and resecting the part on one of the sides. For spherical fullerenes, this procedure allows one to control two parameters: the curvature of the cup and its angular extent. Fig. 2 shows a plot of the quantity  $\Omega_{REL}$  against the number of atoms in the cups, for cups obtained from  $C_{60}$ ,  $C_{240}$ , and  $C_{540}$  fullerenes.

Deviations of over 10% are observed for some of the cups derived from  $C_{540}$ . The deviations show maxima for cups with around half the number of atoms as the closed-cage fullerene from which they were derived. As a cup builds up, the number of multiple reflections inside increases and the deviation increases. However, once a cup starts to close, the entrance decreases in size, and the number of trajectories undergoing multiple reflections goes down. In a series of cups with the same angular extent, the deviations are larger for cups derived from larger fullerenes. Examination of space filling models shows that the concave surface area inside a cup increases as a fraction of the total surface area as the cup becomes larger. For cups derived from  $C_{60}$ , the concave surface inside is small and so are the deviations. We are currently performing trajectory calculations with a realistic potential [16] to determine if any of the features in the experimental data previously assigned to graphite sheets [10] could be cups.

Van der Waals clusters of up to several hundred  $C_{60}$  fullerenes have been studied by Martin et al. [33]. These are examples of objects that show extreme surface roughness. We have calculated collision integrals for a range of fullerene clusters using the exact hard-spheres scattering model for comparison with those estimated using the projection approximation. Calculations were performed for icosahedral geometries suggested by the ‘magic’ numbers observed in the abundance spectrum [33], and for the decahedral and fcc geometries found in the calculations of Wales and coworkers [34]. Fig. 3 shows the relative deviation plotted against the (number of  $C_{60}$  units) $^{-1/3}$ . The deviations are nearly linear on this scale, increasing with the number of  $C_{60}$  units to over 23% for  $(C_{60})_{147}$ . The linear dependence results because the average surface curvature of compact bodies is inversely proportional to their linear dimensions. So this is analogous to other cluster size effects that scale [35] with  $n^{-1/3}$ .

In conclusion, the comparisons presented here show that substantial deviations occur between the collision integrals estimated using the projection approximation and those calculated using an exact hard-spheres scattering model. The deviations are large enough that the features observed experimentally could be assigned to the wrong geometries. The largest deviations occur for geometries with grossly

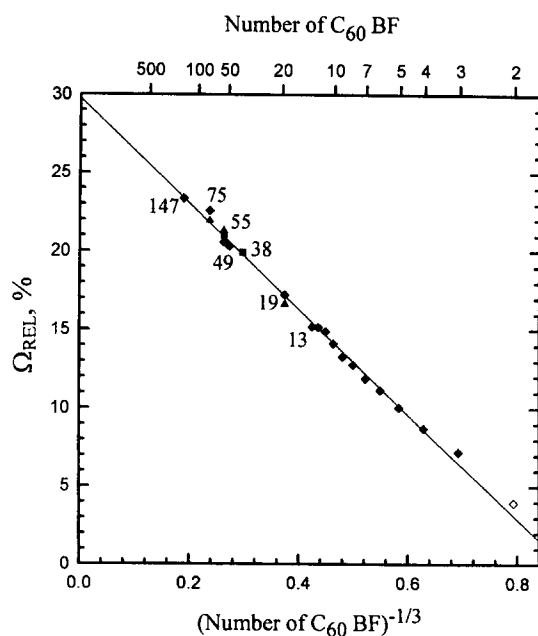


Fig. 3. Plot of the quantity  $\Omega(2.81 \text{ \AA})/P(2.86 \text{ \AA}) - 1$  against the (number of  $C_{60}$  fullerene units) $^{-1/3}$  for clusters with icosahedral growth (rhombi), decahedral geometries (triangles), and fcc geometries (squares). The line is the first-order regression through all the data. The value for the [2+2] cycloaddition  $C_{60}$  dimer is also shown (empty rhombus). The geometry for the dimer is from Strout et al. [37].

concave surfaces where multiple scattering effects are very important. While the most rigorous approach to evaluating the collision integral is to perform trajectory calculations using a realistic potential, this approach requires tremendous amount of computer time as well as information about the intermolecular potential. The exact hard-spheres scattering model described here should be more reliable than the projection approximation employed in previous work, while only slightly more computationally expensive.

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