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# Electrical Mobilities of Multiply-Charged Ionic-Liquid Nanodrops in Air and Carbon Dioxide Over a Wide Temperature Range: Influence of Ion–Induced Dipole Interactions<sup>†</sup>

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The electrical mobilities of hundreds of mass-selected, multiply charged nanodrops (2–6 nm in diameter) of the ionic liquid EMI-BF<sub>4</sub> have been measured in air and CO<sub>2</sub> at temperatures, *T*, ranging from 20 to 100 °C, extending to other temperatures and drift gases previous studies based on EMI-N(CN)<sub>2</sub> nanodrops in air at 20 °C. The known compressibility of EMI-BF<sub>4</sub> removes prior slight ambiguities in the mass-based determination of nanodrop diameters. We confirm the previous finding that the collision cross-sections  $\Omega$  of these nanodrops, inferred from their electrical mobilities, are related to their diameters *d* via a relation of the form  $\Omega \approx \xi \frac{\pi}{4} (d + d_g)^2 (1 + \beta \varepsilon^*) (1 + f(Kn))^{-1}$ , where  $\varepsilon^*$  is the ratio between the polarization and thermal energies of the ion–gas molecule system at contact, f(Kn) is a continuum-correction that vanishes in the free-molecule limit, and the coefficients  $d_g$ ,  $\beta$ , and  $\xi$  are inferred experimentally as functions of temperature and drift gas. We also corroborate prior reports that the drag-enhancement factor  $\xi$ , which remains nearly constant with temperature and drift-gas, exceeds slightly the value  $\xi_m \approx 1.36$  established by Millikan's oil drop measurements. Unexpectedly, the coefficient  $\beta$  shows a significant temperature dependence, suggesting that the ion–gas molecule scattering process is affected by *T*. The effective gas-molecule collision diameter  $d_g$  is seen to decrease with *T*, and takes a value in excess of 0.45 nm in CO<sub>2</sub> at 20 °C, considerably larger than in room-temperature air.

#### 1 Introduction

For a variety of practical reasons, moderately-polarizable molecular drift-gases such as  $N_2$ , air, or  $CO_2$  are becoming more widely-used as alternatives or in addition to He in commercial ion mobility-mass spectrometry (IMS–MS) instruments.<sup>1–9</sup> When working with these gases, however, ion-induced dipole (*polarization*) interactions may increase ion collision cross-sections by up to several percent. Correcting for this effect is therefore important in order to enable the accurate determination of true (i.e., geometric) cross-sections from ion mobility measurements. In a recent article, <sup>10</sup> we investigated the effect of polarization interactions on the collision cross-

Mechanical Engineering and Materials Science Department, Yale University, New Haven, CT 06511, USA. E-mail: juan.fernandezgarcia@yale.edu sections  $\Omega$  of globular ions 2–6 nm in diameter measured in room-temperature air. Based on electrical mobility measurements of multiply-charged nanodrops of the ionic liquid (IL) 1-ethyl, 3-methylimidazolium dicyanamide, EMI-N(CN)<sub>2</sub>, we showed that these effects are accurately accounted by multiplying the cross-section  $\Omega_{SM}$  of an uncharged sphere of the same diameter *d* by a simple factor  $G(\varepsilon^*)$ ,

$$\Omega(d, z) = \Omega_{\rm SM}(d + d_{\rm g}) G(\varepsilon^*) , \qquad (1)$$

where z is the valence of the ion,  $d_g$  is an effective gas-molecule collision diameter, and the function  $G(\varepsilon^*)$  depends exclusively on the ratio  $\varepsilon^*$  of the polarization and thermal energies of the ion–gas molecule system at contact,

$$\varepsilon^*(d+d_{\rm g},z) = \frac{2\alpha \left(ze\right)^2}{\pi \varepsilon_0 kT \left(d+d_{\rm g}\right)^4} , \qquad (2)$$

where  $\varepsilon_0$  is the permittivity of vacuum, *k* is Boltzmann's constant, *T* is the gas temperature, and  $\alpha$  its polarizability. The cross-section  $\Omega_{\text{SM}}$  used in (1) as reference for the uncharged ion is not the customary hard-sphere cross-section  $\Omega_{\text{HS}} = \frac{\pi}{4}(d + d_g)^2$ , but is based instead on the well-known

<sup>†</sup> Electronic Supplementary Information (ESI) available: Three online appendices are supplied, the first dealing with the determination of the Tait equation parameters  $K_0$  and  $k_s$  for EMI-BF<sub>4</sub> at the temperatures considered in the study, the second showing the temperature dependence of the reduced mobility of THA<sup>+</sup> relative to that of 2,6-DtBP<sup>+</sup> in air over the range 20–100 °C, based on IMS–MS measurements carried out in our lab, and the third including plots of  $Z_0/Z_{0,SM,mod}$  vs.  $\varepsilon^*$ , analogous to those in Figure 5 but corresponding to EMI-BF<sub>4</sub> + THABr spectra. See DOI: 10.1039/c4cp000000X

*Stokes–Millikan* (SM) law<sup>11,12</sup> for the mobility of spherical ions. The SM law includes a drag-enhancement factor  $\xi$ ,<sup>12</sup> as well as a continuum-correction factor<sup>10</sup> (see Equation (16b)) that slightly departs from unity for nanometer-sized ions at atmospheric pressure. In the free-molecule limit, the continuum correction vanishes, and

$$\Omega_{\rm SM}(d+d_{\rm g}) = \xi \frac{\pi}{4} (d+d_{\rm g})^2 = \xi \,\Omega_{\rm HS}(d+d_{\rm g}) \,. \tag{3}$$

Our prior study in air at 20 °C<sup>10</sup> comprised IL nanodrops with z = 3-10 and  $d \approx 2-6$  nm, spanning the range 0.05  $< \varepsilon^* < 0.20$ . Based on their measured electrical mobilities, we showed that, when the effective gas-molecule collision diameter was optimally chosen to minimize scattering of the data ( $d_g \approx 0.26$  nm), the polarization correction was well represented by the linear law

$$G(\varepsilon^*) = (1 - \beta \varepsilon^*)^{-1} \approx 1 + \beta \varepsilon^* \qquad \text{(for } \beta \varepsilon^* \ll 1\text{)} \,, \quad (4)$$

with  $\beta \approx 0.36$ . The coefficient  $\xi$  appearing in (3) took the value  $\xi \approx 1.42$ , slightly (~ 5%) larger than Millikan's already substantial drag-enhancement factor  $\xi_m \approx 1.36$ . However, as already noted there, <sup>10</sup> several issues still exist regarding the accuracy and range of applicability of the above values of  $d_g$ ,  $\beta$ , and  $\xi$ .

First, our experimental determination relied on identifying the diameter *d* of each nanodrop with a *mass-based* diameter, defined as that of a sphere with the mass *m* and density  $\rho$  of the nanodrop, with  $\rho$  taken as the bulk density of the IL, corrected for the non-negligible compression due to capillary and electrostatic stresses. In the absence of literature values for the isothermal compressibility coefficients of EMI-N(CN)<sub>2</sub>, we used those available for the IL 1-ethyl, 3-methylimidazolium tetrafluoroborate (EMI-BF<sub>4</sub>) which, despite the expected similarity between both these ILs, propagates some uncertainty in the reported values of  $d_g$ ,  $\beta$ , and  $\xi$ .

Second, our work was limited to a single drift gas (air) at a single temperature (20 °C). Therefore, the validities of the polarization correction (1)–(4) and the corresponding values of  $d_g$ ,  $\beta$ , and  $\xi$  need to be investigated at other temperatures and in other drift gases. In particular, the effective gas-molecule collision diameter  $d_g$ , non-negligible even in He, is expected to be strongly temperature- and gas-dependent. Regarding  $\beta$ and  $\xi$ , model calculations suggest that any temperature- and gas-dependence must have an indirect nature, given by changes in ion–gas molecule scattering dynamics with temperature and drift gas.<sup>13</sup> Hence, measurements at different temperatures and in different drift gases should also shed light on the factors affecting the nature of the scattering process.

Here we extend our measurements to confirm the validity of expressions (1)–(4) over a wider range of temperatures (20–

100 °C) and drift gases (air and CO<sub>2</sub>), and to determine the temperature- and gas-dependence of  $d_g$ ,  $\beta$  and  $\xi$ . In addition, we now rely on nanodrops of the ionic liquid EMI-BF<sub>4</sub>, for which experimental data on compressibility are available, thus removing the slight ambiguities incurred in our prior studies.

### 2 Materials and Methods

#### 2.1 Methods: Tandem DMA-MS

Our IMS–MS system, sketched in Figure 1, has been previously described in detail.<sup>10</sup> Therefore, only a brief review of its main features and other new relevant details will be presented here.

Electrical mobility and mass are measured in series using a parallel-plate Differential Mobility Analyzer (DMA-P4; SEADM, Boecillo, Spain) coupled to a Triple Quadrupole– Time of Flight Mass Spectrometer (QStarXL; MDS Sciex, Concord, ON). A solution of the analyte of interest is electrosprayed in front of the DMA entrance slit, and the charged, pure-analyte nanodrops remaining after solvent evaporation are drawn electrostatically into the DMA against a drift-gas counterflow of some  $0.3 \ 1 \ min^{-1}$ . The DMA acts as a linear mobility filter, transmitting into the atmospheric pressure interface of the MS only those ions with mobilities Z satisfying

$$ZV_{\rm DMA} = Uh^2/L \tag{5}$$

where  $V_{\text{DMA}}$  is the high-voltage difference applied between the DMA's parallel electrodes, L = 4 cm and h = 1 cm are the DMA classification length and inter-electrode distance, and U is the axial drift-gas flow velocity (see inset (b) of Figure 1). The resulting monomobile aerosol beam is then guided by the QStarXL's three quadrupoles (RF-only mode, no mass-selection or fragmentation) into its Time of Flight (TOF) section, where it is mass-analyzed. Scanning over a range of mobilities (i.e., DMA voltages) and performing TOF analysis for each of them yields then a two-dimensional (2D) mass-mobility spectrum of the charged analyte nanodrops.

To maintain a constant drift-gas composition, the DMA is operated in recirculating mode, requiring a continuous make-up drift-gas supply rate of  $0.8 \ l \ min^{-1}$ , to provide the  $0.5 \ l \ min^{-1}$ ingested by the critical orifice at the DMA–MS interface plus the extra  $0.3 \ l \ min^{-1}$  employed as counterflow. The recirculating flow is driven by a modified vacuum blower controlled by an active-stabilization system (SEADM).

The temperature T of the recirculating drift-gas flow is measured upstream of the analysis section of the DMA with a previously calibrated, PID-monitored, type-J thermocouple. This temperature can be regulated in our setup in the range



**Fig. 1** Schematic of the tandem DMA–MS system, and details of (*a*) DMA analysis region, showing its operating principle, and (*b*) interface between ES source and DMA (figure reproduced from prior work<sup>10</sup>)

15–100 °C, with a precision of  $\pm$  0.2 °C around the user-set value, via a water-to-air intercooler fed by a refrigerated recirculator (Neslab CFT-25; Thermo Scientific Neslab, Newington, NH) and a set of PID-controlled electrical heaters, both acting upstream of the thermocouple section. Given the negligible pressure drop across the DMA inlet slit associated to the low counterflow levels used here, the pressure *p* in the analysis section is assumed to be that of the ambient air, which is monitored from local weather stations.

All mobility measurements here reported were performed using either *Ultra-Zero* grade dry air or *Bone-dry* grade CO<sub>2</sub> (Airgas East, Salem, NH) as drift gases. For each gas, measurements were carried out at five different temperatures of 20, 40, 60, 80, and 100 °C.

Mass measurements were performed using the QStarXL's *Enhance All* mode and a focusing potential of 12.5 V, which yielded an optimum signal intensity level. In order to minimize changes in ion composition between the mass and mobility

measurements, both of the instrument's declustering potentials were set to 0 V.

#### 2.2 Materials and Electrospray Ionization (ESI)

Charged nanodrops were produced by electrospraying (in the positive polarity) 20–30 mM solutions of the IL 1-ethyl, 3-methylimidazolium tetrafluoroborate (EMI-BF<sub>4</sub>, purity > 98 %; IoLiTec Ionic Liquids Technologies GmbH, Heilbronn, Germany) in HPLC-grade acetonitrile (ACN; Avantor-J.T. Baker, Center Valley, PA). Like most imidazolium-halide-based ILs,<sup>14</sup> EMI-BF<sub>4</sub> is hygroscopic, and thus all mixtures were prepared after drying the pure IL under vacuum, at room temperature, for some 24 hours, to remove any possible traces of water from it.

Samples of the above solutions were stored in leak-tight 0.5 ml polypropylene vials (DOT Scientific Inc., Burton, MI) and fed from there to the tip of a tapered silica capillary (20  $\mu$ m ID,

360  $\mu$ m OD, 50  $\mu$ m tip OD, 39 cm length; Polymicro Technologies, Phoenix, AZ), from which they were electrosprayed. In order to generate the ES, a palladium wire immersed into the liquid in the vial was raised to a high voltage HV<sub>1</sub>  $\approx$  1.5–2 kV above a facing perforated electrode located approximately 1.5 mm away from the tip and 2 mm upstream of the DMA inlet slit, resulting in the formation of a Taylor cone at the capillary-tip outer diameter. The perforated electrode was then raised to HV<sub>2</sub>  $\approx$  1–1.5 kV above the upper DMA electrode, to drive the positively-charged EMI-BF<sub>4</sub> nanodrops remaining after ACN evaporation into the DMA inlet. The stability of ES operation during the measurements was assessed by monitoring both the Taylor cone (visually) and the current emitted by the ES, which oscillated no more than ±2 % during the whole acquisition of each 2D spectrum.

#### 2.3 DMA Calibration

Based on equation (5), the conversion between DMA voltages and transmitted mobilities would require knowledge of the axial drift-gas velocity U. Nevertheless, since the DMA operates at a fixed velocity, the voltage–mobility correspondence can be simply determined, for a given set of operating conditions (drift gas, pressure, temperature, and blower rotational speed), by measuring the voltage  $V_s$  at which a standard ion of known mobility  $Z_s$  is transmitted by the DMA. The mobility Z of any ion transmitted at a voltage  $V_{\text{DMA}}$  under those same operating conditions is then given by

$$Z = Z_{\rm s} V_{\rm s} / V_{\rm DMA} , \qquad (6)$$

or analogously, in terms of reduced mobilities, as

$$Z_0 = Z_{\rm s0} V_{\rm s} / V_{\rm DMA} , \qquad (7)$$

where the reduced mobility is defined as<sup>15</sup>

$$Z_0 = Z\left(\frac{p}{p_0}\right) \left(\frac{T_0}{T}\right) \tag{8a}$$

 $p_0 = 1 \text{ atm} \quad T_0 = 273.15 \text{ K},$  (8b-c)

with the advantage that the latter does not depend on p.

Similarly to the strategy followed in our prior study,<sup>10</sup> and due to the lack of reliable mobility data for particular EMI-BF<sub>4</sub> nanodrops which could have been used as internal standards, here we adopted once more a two-step mobility-scale calibration approach: for each drift gas / temperature condition investigated, two separate IMS–MS measurements were performed:

First, an ACN-based 20 mM EMI-BF<sub>4</sub> + 5  $\mu$ M tetraheptylammonium bromide (THABr; Sigma-Aldrich, St. Louis, MO) solution was electrosprayed in the positive polarity. The tetraheptylammonium cation THA<sup>+</sup> (m/z = 410.79 Da), with reported mobilities  $Z_s = 0.9709 / 0.6640$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in air / CO<sub>2</sub> at 22 °C and 760 Torr<sup>16,17</sup> (corresponding to reduced mobilities  $Z_{s0} = 0.8995 / 0.6145$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at that temperature, or at any other, under the assumption that  $Z_0$  remains constant with *T* for this ion<sup>18</sup>), was used as internal standard in this measurement. This allowed us, using equation (7), to assign values for the reduced mobilities  $Z_0^i$  (i = 1...N) of a set of *N* well-resolved, pure-EMI-BF<sub>4</sub> nanodrops present in the corresponding IL–THABr spectrum (based on the known reduced mobility of THA<sup>+</sup> and the ratios between the DMA voltages at which THA<sup>+</sup> and each of those nanodrops were transmitted).

After that, and to minimize spectral congestion, THABr was removed, and a pure-IL measurement was performed by electrospraying an ACN-based EMI-BF<sub>4</sub> solution under identical gas-temperature conditions. The *N* reduced mobility values determined from the IL-THABr measurement, together with the *N* DMA voltages  $V_{DMA}^i$  at which the corresponding ions were detected in this pure-IL spectrum, were then used to compute an average DMA calibration constant

$$\langle Z_{\rm s0} V_{\rm s} \rangle = \frac{1}{N} \sum_{\rm i=1}^{N} Z_0^i V_{\rm DMA}^i , \qquad (9)$$

which was then introduced in equation (7), in lieu of  $Z_{s0}V_s$ , for determining the reduced mobilities of all nanodrops present in the pure-IL spectrum.

While this two-step method is formally similar to that introduced in our previous study, <sup>10</sup> its use of a large number of *internal* IL-nanodrop standards (as opposed to a single ion) in the second step of the calibration makes it more reliable. Nonetheless, mobility-scale errors might still arise from uncertainties in the mobility of the THA<sup>+</sup> standard.

#### 3 Results and Discussion

# 3.1 2D Mass-Mobility Spectra and Determination of Nanodrop Mobilities

Figure 2 shows a 2D mass–mobility spectrum of positivelycharged EMI-BF<sub>4</sub> nanodrops, acquired using dry air at 60 °C as the drift gas. This particular measurement will be used to briefly illustrate the features typically observed in 2D mass– mobility spectra of IL nanodrops and the methodology used to infer the effect of polarization. For further details, the reader is referred elsewhere.<sup>10</sup>



**Fig. 2** 2D mass–mobility spectrum of positively-charged EMI-BF<sub>4</sub> nanodrops (drift gas: dry air at 60 °C). White circles indicate the locations of the mobility peaks corresponding to the various nanodrops in the spectrum. *Inset:* zoom into the  $z = 4 \rightarrow 3$  ion evaporation product band, illustrating the approach used to determine the location of the mobility-peak centroid associated with a given ion in the spectrum (and, in this case, its assignment to the correct parent ion)

The abscissa in Figure 2 is the DMA voltage  $V_{\text{DMA}} \propto Z^{-1}$ , while the ordinate is shifted from the mass-to-charge ratio m/z to the equivalent variable

$$n/z = (m/z - m_{\rm i})/m_{\rm o}$$
 (10)

(where  $m_0 = 197.97$  Da and  $m_i = 111.17$  Da are respectively the mean molecular weights of EMI-BF<sub>4</sub> and the EMI<sup>+</sup> cation), and the signal intensity measured by the MS detector at each  $(V_{\text{DMA}}, m/z)$  is represented using a normalized, logarithmic color-scale (indicated in the accompanying color bar). For this particular measurement, the DMA voltage was ramped from 1,840 to 4,500 V in 4 V increments, whereas TOF analysis was performed in the range m/z = 300-10,000 Da, with a dwell time of 2.5 s per DMA voltage.

The conversion from m/z to n/z is meant to simplify the identification of EMI-BF<sub>4</sub> nanodrops within the 2D spectrum. Indeed, since EMI-BF<sub>4</sub> is an ionic substance, any of its positivelycharged nanodrops will have a composition of the form [EMI-BF<sub>4</sub>]<sub>n</sub>[EMI<sup>+</sup>]<sub>z</sub>, with an associated mass  $m = nm_0 + zm_i$ , and thus the variable n/z defined in (10) measures the number of neutral cation–anion pairs per excess cation in a given EMI-BF<sub>4</sub> nanodrop. Note, however, that this *experimental* n/z variable is continuous rather than discrete, since it is derived directly from the high resolution m/z variable measured by the MS.

Among the various features typically observed in massmobility spectra of ILs, the most prominent is perhaps that the signal is separated in a series of *bands* decreasing in mobility with increasing mass. Each of these bands, subsequently denoted as *z*-bands, corresponds to a fixed nanodrop charge state +*z*, with *z* increasing with increasing band height, as indicated in Figure 2 by the labels to the right of each band. This *z*-assignment is confirmed by the fact that each *z*-band is constituted by a series of horizontal *segments* appearing at integer multiples of 1/z in the n/z axis, and which therefore correspond to pure-IL nanodrops of increasing *n* for that given *z*. From here on, and for the sake of brevity, we will refer to such nanodrops simply as  $n^{+z}$ .

Other relevant features commonly found in mass–mobility spectra of ILs can also be distinguished in Figure 2. These include the presence of traces of single and multiple neutral ion-pair (i.e., EMI-BF<sub>4</sub>) evaporation events (signaled by the occurrence of *ladder-like* patterns associated with a majority of the z = 1 and some of the smallest z = 2 nanodrops), as well as of products of dimer ion (i.e., EMI-BF<sub>4</sub>-EMI<sup>+</sup>) evaporation events (evidenced by the appearance of spurious bands of lower z as apparent extensions, towards the left of the spectrum, of the main z-bands). Both of these sorts of evaporation events take place between the mobility and mass measurements.

Once the above spectral features have been identified, the peaks in each of the different regions of the spectrum can be assigned the actual *z* and *n/z* with which their mobility was measured, and the reduced mobilities of the corresponding *parent* ions can be determined following the approach outlined in the inset of Figure 2. The latter consists in adding up, within a certain *z*-region, the signal intensities of all data points associated with a given  $V_{\text{DMA}}$  and located in vicinity  $\pm \Delta n$  (=  $\pm$  0.2 here) of a given integer *n*, and fitting the resulting DMA-voltage distribution to a Gaussian distribution with a baseline. The values  $V_{\text{DMA}}(n, z)$  corresponding to the centroids of the best-fit Gaussians for each of our nanodrops can then be turned into reduced mobilities following the procedure described in the DMA Calibration section of Materials and Methods, which

then yields a  $Z_0(n, z)$  distribution for our whole collection of nanodrops, each of them identified by discrete, integer values of *n* and *z*.

#### 3.2 Mobility-Based Collision Cross-Sections vs. Mass-Based Diameters: Effect of Polarization

The reduced-mobility distribution  $Z_0(n, z)$  for our set of nanodrops can be converted into a collision cross-section distribution  $\Omega(n, z)$  according to the Kinetic Theory relation<sup>15</sup>

$$\Omega(n,z) = \frac{3}{16} \frac{ze}{p_0} \left(\frac{2\pi kT_0}{m_g}\right)^{1/2} \left(\frac{T_0}{T}\right)^{1/2} \left(1 + \frac{m_g}{m(n,z)}\right)^{1/2} \frac{1}{Z_0(n,z)},$$
(11)

where  $m_g$  is the mean molecular mass of the drift-gas, and the (exact) mass *m* of each nanodrop is simply determined as

$$m(n,z) = nm_0 + zm_i . \tag{12}$$

From *m*, on the other hand, and assuming that our nanodrops are approximately spherical, one can define a mass-based diameter  $d_m$  for each of them, corresponding to the diameter of a sphere of the same mass with the density  $\rho$  of the IL matter, as

$$d_{\rm m}(n,z;\rho) = \left(\frac{6m(n,z)}{\pi\rho}\right)^{1/3}$$
 (13)

The sphericity (or near-sphericity) assumption can be justified, for sufficiently large nanodrops, based on the fact that EMI-BF<sub>4</sub> remains liquid even below room temperature, <sup>19</sup> and is corroborated by the results of molecular dynamics simulations.<sup>20</sup> Here, as in prior work, <sup>10</sup> we further take into account the non-negligible compression experienced by such small charged nanodrops as a result of the competing capillary and electrostatic stresses acting over their surfaces, and assume that the density  $\rho$  of each of our nanodrops departs from the bulk density  $\rho_0$  of EMI-BF<sub>4</sub> according the *Tait equation*,<sup>21,22</sup>

$$\frac{\rho_{\rm o}}{\rho} = 1 - \frac{\Delta p}{K_{\rm o} + k_{\rm s} \Delta p} , \qquad (14)$$

where the isothermal compressibility coefficients  $K_o$  and  $k_s$  are functions of the temperature, and  $\Delta p$  is the net overpressure (relative to the surrounding atmosphere) acting over a given nanodrop due to capillary and electrostatic forces. Assuming a polar or perfectly-conducting spherical droplet of charge q = ze, diameter  $d_m$ , and surface tension  $\gamma$ , the latter can be written as

$$\Delta p = p_{\text{cap}} - p_{\text{elec}} = \frac{4\gamma}{d_{\text{m}}} - \frac{(ze)^2}{2\pi^2 \varepsilon_0 d_{\text{m}}^4} \,. \tag{15}$$

Provided that  $\rho_0$ ,  $\gamma$ ,  $K_0$ , and  $k_s$  are known for our IL (see Table 1), the set of equations (12) – (15) can be solved for  $d_{\rm m}$  for all our nanodrops which, in turn, enables performing a comparison between their *experimentally-derived* collision cross-sections and *theoretical* mass-based diameters. Figure 3 shows a plot of the theoretical mass-based diameter versus the experimentallydetermined collision cross-section for positively-charged EMI-BF<sub>4</sub> nanodrops with z = 1-8 in dry air at 60 °C (data on the right, open circles, labeled  $d_{Z,HS}$ ), corresponding to the data in the 2D spectrum of Figure 2. The abscissa there is not strictly  $\Omega$ , but the analogous variable  $d_{Z,HS} = (4\Omega/\pi)^{1/2}$ , representing the equivalent hard-sphere diameter for a given collision cross-section, whereas the ordinate is just  $d_{\rm m}$ . Notice that the data for charge states z = 9 and 10, although present in Figure 2, have not been included in Figure 3. This is because the signal intensity associated with those higher charge states decreased progressively as the drift gas temperature was increased, precluding an accurate determination of the mobilities of the corresponding nanodrops for the highest temperatures investigated here. Thus, in order to use the same set of charge states in measurements corresponding to different temperatures, we have ignored nanodrops with z = 9-10 in the analysis of all our measurements. Similarly, all nanodrops with associated ion-peak resolutions (based on the full width at half maximum of the corresponding best-fit Gaussians) below or above certain arbitrarily-set thresholds (chosen here respectively as 30 and 90, based on the typical resolution of  $\sim$  60 for our DMA) have also been removed from all further analysis.

Two observations worthy of mention can be drawn from the  $d_{Z,HS}$  vs.  $d_m$  data in Figure 3. The first is evidenced by the results of performing linear least-squares regression of the data to a model of the form  $d_{Z,HS} = \xi^{1/2} (d_m + d_g)$  (dashed line), which yields here the best-fit coefficients  $d_g = 0.254$  nm and  $\xi = 1.3911$ . The latter corresponds to an effective collision cross-section increase (or *drag enhancement*) of ~39% over that for rigid, smooth hard-spheres of the same diameter, for which  $\Omega = \Omega_{HS} = \frac{\pi}{4} (d_m + d_g)^2$ . This number, in relatively good agreement with the room-temperature air results of our prior work, <sup>10</sup> as well as with those of earlier studies from our group involving singly- and multiply-charged globular ions in room-temperature air and CO<sub>2</sub>, <sup>3,20,23,24</sup> suggests that the mobilities of our nanodrops are moderately well represented by the so-called *modified* Stokes–Millikan law <sup>11,12,25</sup> which, when expressed in terms of reduced mobilities, reads<sup>10</sup>

$$Z_{0,SM,mod}(d + d_{g}, z, m) = \frac{3}{16} \frac{ze}{p_{0}} \left(\frac{2\pi kT_{0}}{m_{g}}\right)^{1/2} \left(\frac{T_{0}}{T}\right)^{1/2} \left(1 + \frac{m_{g}}{m}\right)^{1/2} \frac{(1 + f(Kn))}{\xi_{m} \frac{\pi}{4} \left(d + d_{g}\right)^{2}}$$
(16a)

$$f(\text{Kn}) = \frac{1/\text{Kn} + 0.4 \left(e^{-1.1/\text{Kn}} - 1\right)}{1.657}$$
(16b-d)  
$$\text{Kn} = \frac{2\lambda}{d + d_{\text{g}}} \qquad \mu/\lambda = 0.499 p \left(\frac{8m_{\text{g}}}{\pi kT}\right)^{1/2},$$

where the mean free-path  $\lambda$  is defined in terms of the drift-gas viscosity coefficient  $\mu$ , and  $\xi_m = 1.3552$  is the (previously introduced) Millikan drag-enhancement factor. As mentioned earlier, when taken to the free-molecule limit Kn  $\gg 1$ , the continuum correction factor f(Kn) vanishes, and (16a) corresponds to a collision cross-section  $\Omega_{SM} = \xi_m \Omega_{HS}$ , ~36% higher than the respective hard-sphere value, not far from our observations.

The second observation comes from the small but systematic *misalignment* observed in Figure 3 between the  $d_{Z,HS}$  vs.  $d_m$ data corresponding to different z's, particularly apparent in the regions of overlap of consecutive charge states (see inset). This mismatch implies a slight dependence of  $\Omega$  on z for our nanodrops. As shown in the past, 10 such z-dependence can be attributed to the existence of long-range ion-induced dipole interactions acting between our charged nanodrops and the neutral (but moderately polarizable) drift-gas molecules, since  $\Omega$  would then increase with the dimensionless polarizationparameter  $\varepsilon^*$  defined in Equation (2), <sup>15,26,27</sup> in agreement with the behavior observed in Figure 3 (where  $\Omega$  increases with z for a given  $d_{\rm m}$ ). In order to quantify the effect of polarization, and on the basis of the otherwise fair agreement observed between the mobilities of our nanodrops and those predicted by SM, we assume that this effect can be accounted by a law of the form

$$Z_0 = Z_{0,\text{SM,mod}} \cdot g(\varepsilon^*) , \qquad (17)$$

where g is a certain function that depends exclusively on  $\varepsilon^*$ . The form of  $g(\varepsilon^*)$  can then be determined by plotting the ratio  $Z_0/Z_{0,SM,mod}(d_m + d_g, z, m)$  as a function of  $\varepsilon^*(d_m + d_g, z)$ , using the available  $(Z_0, d_m, z, m)$  data for all our nanodrops, and choosing the value of  $d_g$  as that leading to the best "collapse" of the data for the different *z*'s into a single curve in the  $Z_0/Z_{0,SM,mod}$  vs.  $\varepsilon^*$  plane.

Figure 4 shows such a plot for the positively-charged EMI-BF<sub>4</sub> nanodrops of Figure 3, corresponding to the value  $d_g =$  0.212 nm leading to the best collapse of the data for charge states z = 4-8 into a single curve for this particular drift gastemperature condition (air at 60 °C). Also shown there (see inset) is the same plot for  $d_g = 0.26$  nm (the value found in our prior work for room-temperature air<sup>10</sup>), evidencing the sensitivity of the method used for determining  $d_g$ . As done in the past, <sup>10</sup> charge states z = 1 and 2 are ignored for the purpose of selecting the *best-collapse*  $d_g$ , due to the fact that the associated nanodrops in our mass-mobility spectra typically comprise too few neutral ion-pairs (at most 12 and 28 in



**Fig. 3** *Right:* Equivalent hard-sphere mobility diameter  $d_{z,HS}$  vs. mass-based diameter  $d_m$  for positively-charged EMI-BF<sub>4</sub> nanodrops with z = 1-8 in dry air at 60 °C (open circles), and best linear fit  $d_{Z,HS} = \xi^{1/2} (d_m + d_g)$  (dashed line) . *Left:* Polarization-corrected Stokes–Millikan mobility diameter  $d_{Z,pol}$  vs. mass-based diameter  $d_m$  for the same nanodrops (closed circles), and best linear fit with unit slope  $d_{Z,pol} = d_m + d_g$  (solid line). *Inset:* zoom to charge states z = 3-5, evidencing the effect of polarization (right) and the excellent alignment of the different z's upon correcting it (left)

this particular measurement). This raises questions not only about the sphericity<sup>20</sup> of such nanodrops, but also about the feasibility of applying to them concepts such as *surface tension* or *bulk density* which, in turn, would result in their mass-based diameter  $d_m$  being ill-defined. In addition, and for reasons analogous to those discussed earlier regarding charge states z = 9 and 10 (i.e., for consistency between the results of the various measurements here presented), nanodrops with z = 3are also ignored for this purpose. As it will become clear later, these nanodrops depart from the trend established by the higher charge states at some of the temperatures included in our study.

As made evident by Figure 4, the data for z = 4-8 not only fall into a single curve, but are further aligned into a straight line, showing that the function  $g(\varepsilon^*)$  is approximately linear in  $\varepsilon^*$  over the range of  $\varepsilon^*$  spanned by our data, and can thus be modeled as

$$g(\varepsilon^*) \approx (\xi_{\rm m}/\xi) (1 - \beta \varepsilon^*)$$
 (18)

Performing linear least-squares regression of the data in Figure 4 with z = 4-8 and  $0.07 \le \varepsilon^* \le 0.11$  to a model of the form (18) (dashed line, turned into a solid line over the above

mentioned range of  $\varepsilon^*$ ) yields in turn the values  $\xi = \xi_m/0.9710 = 1.3957$  and  $\beta = 0.419$ . The reason for limiting the lower end of the  $\varepsilon^*$ -range over which linear regression is carried out has its origin in the method we use for determining the bestcollapse  $d_g$  for a given set of data. The method consists in automatically sweeping over  $d_g$  in 0.001 nm steps, plotting the corresponding  $Z_0/Z_{0,\text{SM,mod}}$  vs.  $\varepsilon^*$  data, and performing linear regression until the value of  $d_g$  that maximizes the coefficient of determination of the fit  $R^2$  is found. Since the data for low  $\varepsilon^*$  is typically characterized by a larger scatter (as clearly seen in Figure 4), including them in the regression usually leads to false positives, in the sense of values of  $d_g$  for which, even though  $R^2$  is maximum, the *visual* collapse of the different *z*'s is not optimum.

To confirm the consistency of the proposed polarizationcorrection factor (18) and the values of  $\beta$  and  $\xi$  determined from linear regression, we use these values and our  $(Z_0, z, m)$  data to solve the non-linear equation  $Z_0 = Z_{0,\text{SM,mod}}(d_{Z,\text{pol}}, z, m)$   $(\xi_m/\xi)$   $(1 - \beta \varepsilon^*(d_{Z,\text{pol}}, z))$  for a *polarization-corrected mobility diameter*  $d_{Z,\text{pol}}$  for each of our



**Fig. 4** Plot of  $Z_{0,SM,mod}$  vs. polarization parameter  $\varepsilon^*$  for positively-charged EMI-BF<sub>4</sub> nanodrops with z = 1-8 in dry air at 60 °C, for  $d_g = 0.212$  nm, and best linear fit  $Z_0/Z_{0,SM,mod} = (\xi_m/\xi)(1 - \beta\varepsilon^*)$  in the range  $0.07 \le \varepsilon^* \le 0.11$  for nanodrops with z = 4-8. Closed and open circles represent respectively nanodrops included and not included in the linear regression. *Inset:* comparison with the same plot for  $d_g = 0.260$  nm, showing the lack of collapse of the various *z*'s

nanodrops and, as done earlier with  $d_{Z,HS}$ , compare the latter with their theoretically-determined mass-based diameters  $d_{\rm m}$ . A plot of  $d_{Z,pol}$  as a function of  $d_m$  is shown in Figure 3 (data on the left, closed circles), showing that such experimentallydetermined, polarization-corrected diameters indeed match the expected behavior  $d_{Z,pol} = d_m + d_g$ , falling into a single line of unit slope and intercept  $d_g = 0.209$  nm. Furthermore, the data thus corrected show no more apparent misalignments between the various z's, hence confirming the results of our analysis. Note that a slight  $(\sim 1\%)$  discrepancy exists between the value of  $d_g = 0.212$  nm, found earlier based on the best-collapse criterion, and that of  $d_g = 0.209$  nm derived from the  $d_{Z,pol}$  vs.  $d_{\rm m}$  regression. This difference, inconsequential in any case, arises from the fact that all z's for which data is available (i.e., z = 1-8) are included in the latter regression, whereas only nanodrops with z = 4-8 were considered for determining  $d_{g}$ earlier.

# **3.3** Extension of the Analysis to a Wider Range of Temperatures and Drift Gases

As indicated in the Materials and Methods section, the analysis just presented was repeated using both air and CO<sub>2</sub> as drift gases, at temperatures of 20, 40, 60, 80, and 100 °C. The values for the relevant properties of EMI-BF<sub>4</sub>, air, and CO<sub>2</sub> used in our analysis at each of these temperatures are listed in Table 1, together with the references to the literature from which they originate. In addition, the values  $\alpha_{Air} = 1.70 \text{ Å}^{3\,28}$  and  $\alpha_{CO_2} = 2.60 \text{ Å}^{3\,29}$  were used for the polarizabilities of air and CO<sub>2</sub> (at all temperatures). As mentioned earlier, only charge states z = 1-8 were taken into account in the analysis of all spectra, with z = 1-3 being further ignored for the purpose of determining the best-collapse  $d_g$ , as well as the values of  $\beta$  and  $\xi$  derived from linear least-squares regression of the  $Z_0/Z_{0,SM,mod}$  vs.  $\varepsilon^*$  data.

Figure 5 includes plots of  $Z_0/Z_{0,SM,mod}$  vs.  $\varepsilon^*$ , analogous to that in Figure 4, for all drift gas-temperature conditions investigated in our study. As evidenced there, the appropriate choice of  $d_g$  for every given drift gas-temperature combination

**Table 1** Values of the bulk density  $\rho_0$ , surface tension  $\gamma$ , and isothermal compressibility coefficients  $K_0$  and  $k_s$  for EMI-BF<sub>4</sub>, and of the viscosity  $\mu$  and mean free-path  $\lambda$  of air and CO<sub>2</sub>, at the temperatures investigated. The values for  $K_0$  and  $k_s$  were determined by fitting ( $\rho$ , p, T) data for EMI-BF<sub>4</sub> reported in the literature<sup>30</sup> to the Tait equation (see Electronic Supplementary Information, Appendix A), those for  $\mu$  were found according to the Kinetic Theory of viscosity, <sup>31</sup> and those for  $\lambda$  were computed using Equation (16d), assuming p = 1 atm.

| T (°C)  | 20            | 40            | 60            | 80            | 100           |
|---|---------------|---------------|---------------|---------------|---------------|
| $ \frac{\rho_{\rm o} \ (\rm kg \ m^{-3})^{30}}{\gamma \ (\rm mN \ m^{-1})^{32}} \\ K_{\rm o} \ (\rm GPa)^{30} $ | 1284.4        | 1269.1        | 1254.0        | 1239.3        | 1225.0        |
|   | 54.29         | 53.01         | 51.74         | 50.47         | 49.20         |
|   | 2.90          | 2.73          | 2.56          | 2.39          | 2.32          |
| $k_{\rm s}^{30}$  | 4.80          | 4.78          | 4.76          | 4.73          | 4.70          |
| $ \mu_{\text{Air/CO}_2} (\mu \text{Pa s})^{31} \\ \lambda_{\text{Air/CO}_2} (\text{nm})^{\text{Eq. (16d)}} $    | 18.14 / 14.61 | 19.06 / 15.52 | 19.96 / 16.40 | 20.84 / 17.27 | 21.69 / 18.11 |
|   | 65.20 / 42.62 | 70.84 / 46.79 | 76.51 / 51.01 | 82.22 / 55.28 | 87.97 / 59.60 |

yields in all cases a good collapse of the  $Z_0/Z_{0.SM,mod}$  vs.  $\varepsilon^*$ data for z = 4-8 (and even for z = 3, in a majority of cases, but read below) into a single curve. Furthermore, the data are still aligned along a straight line, thus validating the linear form of  $g(\varepsilon^*)$ , over the whole range of  $\varepsilon^*$  covered by the data for both air and CO<sub>2</sub>, at all temperatures investigated except for 100 °C. A slight *bend* is observed in the low- $\varepsilon^*$  end for both gases at 100 °C. This apparent departure from linearity, which should be investigated in more detail, seems a priori to be related to the increase in drift-gas temperature rather than to the decrease in  $\varepsilon^*$ , since the associated bend in  $g(\varepsilon^*)$ is not observed for the data at 80 °C, which extend in both gases to values of  $\varepsilon^*$  nearly as low as those reached by the corresponding 100 °C data. In the present study, the above mentioned issue was simply dealt with by limiting the ranges of  $\varepsilon^*$  used for regression of the data for the two 100 °C samples to those intervals over which  $g(\varepsilon)$  is distinctly linear in each of them. In any case, and as mentioned earlier, we must note that the lower end of this  $\varepsilon^*$ -range is limited too for the remaining samples, in order to prevent the higher scatter of the low- $\varepsilon^*$  data from biasing our automated determination of the best-collapse  $d_{\rm g}$ . Finally, note the previously mentioned departure of the data for z = 3 from the trend established by the higher charge states, particularly evident in air at the higher temperatures included in our study (60–100 °C), whence nanodrops with z = 3 have been ignored in our analysis at all temperatures. This departure is most notorious in the high- $\varepsilon^*$  end, associated with the smallest nanodrops of that charge state (comprising here down to some 30 neutral ion-pairs). Such behavior, reminiscent of that of charge states z = 1, 2 at all temperatures, suggests again a lack of sphericity of these smallest nanodrops. Despite the weaker manifestation of this departure in CO<sub>2</sub> than in air, which could cast some doubts on this non-sphericity hypothesis, the anomaly appears in any case to be clearly associated to small sizes.

The best fits of the data for each drift gas-temperature condition to a linear model of the form (18) are represented in Figure 5 using again dashed lines, with the associated values of  $d_g$ ,  $\beta$ , and  $\xi$  listed in Table 2, together with the ranges of  $\varepsilon^*$  over which linear regression was performed for each particular sample. Also included in Table 2 are analogous results derived from analyzing the EMI-BF<sub>4</sub> + THABr data collected for DMA-calibration purposes (see DMA Calibration section under Materials and Methods) over an identical set of drift gastemperature combinations, with the corresponding  $Z_0/Z_{0 \text{ SM mod}}$ vs.  $\varepsilon^*$  plots (analogous to those in Figure 5) shown in Appendix C of the Electronic Supplementary Information. The values of  $d_g$ ,  $\beta$ , and  $\xi$  resulting from averaging those determined in each pair of measurements (i.e., with and without THABr) for every given gas-temperature condition are also listed in Table 2. Finally, plots of all of the above mentioned values of  $d_{g}$ ,  $\beta$ , and  $\xi$ , as a function of temperature, and for each of the two drift gases investigated, can be found in Figure 6.

# **3.4** Comments on the Drift-gas and Temperature Dependence of the Parameters *d*<sub>g</sub>, *β*, and *ξ*

The results just presented corroborate and, furthermore, extend the range of applicability of the conclusion reached in our prior work in room-temperature air: The (reduced) mobilities of near-spherical, multiply-charged IL nanodrops of diameter *d*, charge q = ze, and mass *m*, in molecular drift gases with moderate polarizabilities, are accurately represented by a modified version of the Stokes–Millikan law, corrected to include the effect of ion–induced dipole interactions, of the form

$$Z_{0} = Z_{0,\text{SM,mod}}(d + d_{g}, z, m) \cdot (\xi_{m}/\xi) \cdot (1 - \beta \varepsilon^{*})$$

$$\varepsilon^{*} = \frac{2\alpha (ze)^{2}}{\pi \varepsilon_{0} kT \left(d + d_{g}\right)^{4}} , \qquad (19a-b)$$

where  $Z_{0,\text{SM,mod}}$  is given in Equation (16),  $\xi_{\text{m}} = 1.3552$  is Millikan's drag enhancement factor, and  $d_{\text{g}}$ ,  $\beta$ , and  $\xi$  are empirically-determined parameters which, based on the results of our analysis, depend (to a greater or lesser extent) on



**Fig. 5** Plots of  $Z_0/Z_{0,SM,mod}$  vs. polarization parameter  $\varepsilon^*$  for positively-charged EMI-BF<sub>4</sub> nanodrops with z = 1-8, in dry air (left) and CO<sub>2</sub> (right), at temperatures of 20, 40, 60, 80, and 100 °C (increasing from top to bottom), corresponding to the best-collapse  $d_g$  in each case, and best linear fits for nanodrops with z = 4-8 (same colors and symbols as in Figure 4). The range of  $\varepsilon^*$  over which each sample was fitted, and the associated best-fit values of  $d_g$ ,  $\beta$ , and  $\xi$ , are listed in Table 2

**Table 2** Values of  $d_g$ ,  $\beta$ , and  $\xi$  determined for every gas-temperature condition investigated, for measurements performed with or without THABr (see last column), together with the ranges of  $\varepsilon^*$  over which linear regression was performed in each case. The values within angle brackets ( $\langle \rangle$ ) result from averaging the values of  $d_g$ ,  $\beta$ , and  $\xi$  determined in each pair of measurements (with and without THABr) carried out for a given gas-temperature combination.

| Gas             | T (°C) | $d_{\rm g}$ (Å) | $\langle d_{\rm g} \rangle$ (Å) | β              | $\langle \beta \rangle$ | ξ                | $\langle \xi \rangle$ | $\varepsilon^*$ -range  | THABr?       |
|-----------------|--------|-----------------|---------------------------------|----------------|-------------------------|------------------|-----------------------|---|--------------|
| Air             | 20     | 2.42<br>2.49    | 2.46                            | 0.360<br>0.355 | 0.358                   | 1.4266<br>1.4221 | 1.4244                | $\begin{array}{c} 0.083 - 0.135 \\ 0.061 - 0.134 \end{array}$ | $\checkmark$ |
|                 | 40     | 2.26<br>2.32    | 2.29                            | 0.367<br>0.373 | 0.370                   | 1.4150<br>1.4095 | 1.4123                | 0.078 - 0.124<br>0.075 - 0.123                                | $\checkmark$ |
|                 | 60     | 2.12<br>2.17    | 2.15                            | 0.419<br>0.420 | 0.420                   | 1.3957<br>1.3916 | 1.3937                | 0.068 - 0.109<br>0.065 - 0.106                                | $\checkmark$ |
|                 | 80     | 2.06<br>2.11    | 2.09                            | 0.442<br>0.447 | 0.445                   | 1.3770<br>1.3736 | 1.3753                | 0.058 - 0.091<br>0.060 - 0.089                                | $\checkmark$ |
|                 | 100    | 1.91<br>1.86    | 1.89                            | 0.507<br>0.485 | 0.496                   | 1.3582<br>1.3632 | 1.3607                | 0.055 - 0.075<br>0.054 - 0.077                                | $\checkmark$ |
| CO <sub>2</sub> | 20     | 4.61<br>4.50    | 4.56                            | 0.367<br>0.354 | 0.361                   | 1.3824<br>1.3917 | 1.3871                | 0.098 - 0.157<br>0.093 - 0.156                                | $\checkmark$ |
|                 | 40     | 3.98<br>4.00    | 3.99                            | 0.384<br>0.361 | 0.373                   | 1.4141<br>1.4160 | 1.4151                | 0.085 - 0.150<br>0.090 - 0.149                                | $\checkmark$ |
|                 | 60     | 3.66<br>3.66    | 3.66                            | 0.416<br>0.356 | 0.386                   | 1.4228<br>1.4307 | 1.4268                | 0.078 - 0.134<br>0.080 - 0.132                                | $\checkmark$ |
|                 | 80     | 3.42<br>3.46    | 3.44                            | 0.428<br>0.383 | 0.406                   | 1.4280<br>1.4306 | 1.4293                | 0.075 - 0.109<br>0.070 - 0.113                                | $\checkmark$ |
|                 | 100    | 3.25<br>3.26    | 3.26                            | 0.447<br>0.394 | 0.421                   | 1.4293<br>1.4338 | 1.4316                | 0.068 - 0.100<br>0.065 - 0.100                                | $\checkmark$ |

the drift-gas and temperature under consideration. This last section will be devoted to discussing such dependence.

#### Comments about $d_g$ :

The effective gas-molecule collision diameter  $d_g$  is seen to decrease monotonically with temperature in both air and CO<sub>2</sub>. This agrees with the intuitively-expected deeper *penetration* of the more highly-energetic gas molecules into the surface of the nanodrops upon contact.

Another important issue is whether or not  $d_g$  depends on the composition of the surface of the ion. In this sense, the average value of  $\langle d_g \rangle = 0.246$  nm found here for air at 20 °C is ~ 5% lower than the mean value of 0.26 nm found in our prior work,<sup>10</sup> under identical conditions, but based on measurements of EMI-N(CN)<sub>2</sub> nanodrops. For the practical purpose of determining a true ion cross-section by correcting for  $d_g$ , a difference of 0.014 nm is entirely inconsequential, and thus the comparison of the results obtained for these two ILs suggests that  $d_g$  may be provisionally taken as relatively independent of the atomic nature of the target surface. On top of that, such slight difference in  $d_g$  could be due to the use of compressibility data for EMI-BF<sub>4</sub> in the determination of mass-based diameters for EMI-N(CN)<sub>2</sub> nanodrops in the past.<sup>10</sup> As argued in Appendix D of our former study,<sup>10</sup> this assumption should have led to an overestimation of both the compressibility of EMI-N(CN)<sub>2</sub> and the resulting value of  $d_g$ . Finally, it is also possible that the less stringent dryness of the air used in our previous study (up to 7 ppm water content versus up to 2 ppm here) could have increased the probability of water absorption on some of the ions, leading to an apparent increase of  $d_g$ .

In the case of CO<sub>2</sub>, the only prior determination of  $d_g$  we are aware of in which the effect of polarization was taken into account is that by our own group based on measurements of negatively-charged poly(ethylene glycol) ions at 22 °C,<sup>24</sup> in which a value of  $d_g \approx 0.425$  nm was found. Compressibility effects were, however, not taken into consideration in that study and, again, this leads in all cases to an underestimation of  $d_g$ ,<sup>10</sup> which would easily explain the ~7% discrepancy relative to the newly determined value of  $\langle d_g \rangle \approx 0.456$  nm. Note finally that both values are higher than the corresponding Lennard-Jones collision diameter for CO<sub>2</sub>,  $\sigma_{CO_2} = 0.3996$  nm.<sup>31</sup> This



**Fig. 6** Values of  $d_g$ ,  $\beta$ , and  $\xi$  in dry air (left) and CO<sub>2</sub> (right) as a function of temperature, corresponding to measurements performed with or without THABr (open and closed symbols, respectively), and average values considering each pair of measurements carried out for every given gas-temperature combination (solid lines). Note the different scales used in the ordinate of each of the two plots

behavior, in contrast with that previously observed in air (for which  $d_g$  is significantly lower than  $\sigma_{Air} = 0.3617$  nm at all temperatures investigated) could be in part due to the higher polarizability of CO<sub>2</sub>, which would promote its clustering with the target ions,<sup>33</sup> therefore resulting in an apparently larger effective collision diameter. The expected reduction in ion–CO<sub>2</sub> clustering probability with increasing temperature<sup>33</sup> would also explain why the relative decrease of  $d_g$  with *T* is higher in CO<sub>2</sub> than in air.

#### Comments about $\beta$ :

The average values  $\langle \beta \rangle \approx 0.36$  determined here at room temperature for both air and CO<sub>2</sub> coincide with that previously determined for room-temperature air<sup>10</sup> (even though, analogously to  $d_g$ , the latter could have been affected by the more-than-likely overestimation of EMI-N(CN)<sub>2</sub>'s compressibility there). We observe, however, an a priori unexpected behavior for  $\beta$ , in the form of a significant increase of its value with temperature. Model calculations predict that, if the scattering dynamics of the ion–gas molecule system were independent of *T*, then both  $\beta$  and  $\xi$  would also be independent of temperature.

Our observation that  $\beta$  (and, to a much lesser extent as we will soon discuss, also  $\xi$ ) varies with temperature therefore suggests that the scattering dynamics are temperature-dependent in our system. While this behavior would not be at all unreasonable, it is noteworthy that the upper bound of  $\beta$  found in available model calculations of the mobilities of spherical ions under a polarization potential <sup>13,27,34</sup> is 0.36, exactly the lower bound of the values determined experimentally in the present work.

Notice that, based on the values of  $\langle \beta \rangle$  found by averaging the results of our measurements with and without THABr, there seems to be a difference in the rate of increase of  $\beta$  with temperature between air and CO<sub>2</sub>, this increase being sharper in the former than in the latter. There is also, however, a clearly larger disparity in  $\beta$  between the two sets of experiments performed using CO<sub>2</sub> as the drift gas than in those carried out in air. We have reasons to believe that this disparity could be due to the CO<sub>2</sub> measurements with THABr having been performed at a moderately lower drift velocity, which would have led to an increase in space charge effects that, in turn, would explain the lower values of  $\beta$  determined from those measurements (see the discussion about  $\beta$  in our prior work <sup>10</sup>). Indeed, considering only the non-THABr results would lead to a much better agreement between the  $\beta$  vs. *T* behavior in air and CO<sub>2</sub>.

#### Comments about $\xi$ :

The drag-enhancement factor  $\xi$  is the parameter less affected by temperature variations, with values always lying in the range 1.36–1.43 over all drift-gas–temperature conditions investigated, in moderately-good agreement with Millikan's drag enhancement factor  $\xi_m \approx 1.36$ . In particular, the value  $\langle \xi \rangle =$ 1.4244 found here for air at 20 °C agrees with the value  $\langle \xi \rangle =$ 1.42 previously found under identical conditions.<sup>10</sup> We observe, in any case, a systematic variation of the drag-enhancement factor with temperature in both gases, with  $\langle \xi \rangle$  decreasing monotonically with *T* for air, while increasing (also monotonically) with temperature in the case of CO<sub>2</sub>.

Focusing for the time being in the behavior in air, we find that  $\langle \xi \rangle$  decreases some 5% (from ~1.42 to ~1.36) over the entire range of temperatures studied. Because  $\xi$  is directly affected by errors in DMA calibration, <sup>10</sup> this small decrease could then be partly due to the reduced mobility of the tetraheptylammonium cation (THA<sup>+</sup>, the standard used in our experiments) not being as strictly temperature-independent as reported in the literature.<sup>18</sup> We have, in fact, carried out IMS–MS measurements in air over the temperature range 20-100 °C, comparing the mobility of THA<sup>+</sup> with that of the protonated 2,6-di-tert-butyl pyridine cation (2,6-DtBP<sup>+</sup>), whose reduced mobility in air has also been reported to remain constant with temperature.<sup>35</sup> These data show that, if  $Z_0$  was indeed independent of T for 2,6-DtBP<sup>+</sup>, then the reduced mobility of THA<sup>+</sup> would slightly (but monotonically) decay with temperature (see Electronic Supplementary Information, Appendix B), with a ~2.5% reduction upon increasing T from 20 to 100 °C. In this scenario, taking the value  $\langle \xi \rangle \approx 1.42$  found at 20 °C as a fixed reference, would shift the value of  $\langle \xi \rangle$  determined from our experiments at 100 °C from ~1.36 to ~1.395, resulting now in a variation of  $\langle \xi \rangle$  of only ~2% throughout the whole range of temperatures investigated.

Moving on now to CO<sub>2</sub>, it is important to point out that the mobilities determined here at temperatures different from 20 °C have relied on assumption that  $Z_0$  is independent of temperature for the THA<sup>+</sup> cation. This assumption is an extrapolation of the behavior reported in air, <sup>18</sup> with no experimental support in the case of CO<sub>2</sub>. Our mobility-scale calibration in CO<sub>2</sub> is therefore uncertain for temperatures other than 20 °C. <sup>16</sup> The same uncertainty therefore applies to the corresponding values of  $\xi$  reported before. These uncertainties, however, have no impact whatsoever on the values determined for the parameters  $d_g$  and  $\beta$ ). The fact that  $\langle \xi \rangle$  increases with temperature in CO<sub>2</sub>, in qualitative disagreement with our findings in air, represents

an additional reason to suspect of the constant- $Z_0$  assumption adopted for THA<sup>+</sup> in CO<sub>2</sub>. Nevertheless, and despite this qualitative discrepancy, the comparable values found here for  $\langle \xi \rangle$  at room temperature in both air and CO<sub>2</sub>, coupled to the weak temperature-dependence of the former in air, suggests that a similar behavior is to be expected in the case of CO<sub>2</sub>. In any case, IMS measurements analogous to those performed with 2,6-DtBP<sup>+</sup> in air (i.e., using a standard of known reduced mobility vs. *T* in CO<sub>2</sub>, in conjunction with THA<sup>+</sup>) would need to be carried out in order to confirm this thesis.

### 4 Conclusions

We have confirmed and extended to other temperatures and drift gases our prior conclusion for room-temperature air that the (reduced) mobilities  $Z_0$  of near-spherical, multiply-charged IL nanodrops in polarizable, molecular drift gases are accurately represented by a modified version of the Stokes–Millikan law, corrected to include the effect of ion–induced dipole interactions,

$$Z_{0} = Z_{0,\text{SM,mod}}(d + d_{g}, z, m) \cdot (\xi_{m}/\xi) \cdot (1 - \beta \varepsilon^{*})$$

$$\varepsilon^{*} = \frac{2\alpha (ze)^{2}}{\pi \varepsilon_{0} kT \left(d + d_{g}\right)^{4}} , \qquad (20a-b)$$

where *d* is the nanodrop diameter, q = ze its charge, *m* its mass,  $Z_{0,\text{SM,mod}}$  is the modified SM law,  $\xi_m = 1.3552$  is Millikan's drag enhancement factor, and  $d_g$ ,  $\beta$ , and  $\xi$  are empirically-determined parameters. In the limit  $\beta \varepsilon^* \ll 1$  (as is the case for all our nanodrops), Equation (20) corresponds to a collision cross-section of the form

$$\Omega \approx \xi \frac{\pi}{4} \left( d + d_{\rm g} \right)^2 \left( 1 + \beta \varepsilon^* \right) \left( 1 + f({\rm Kn}) \right)^{-1} , \qquad (21)$$

increasing linearly with the polarization parameter  $\varepsilon^*$ , and where f(Kn) (given in (16b)) is a continuum correction ( $\ll 1$  for nanodrops at atmospheric pressure) that vanishes in the free-molecule limit.

The values of the coefficients  $d_g$ ,  $\beta$ , and  $\xi$  in air and CO<sub>2</sub> have been determined based on IL nanodrop IMS–MS measurements performed over the range of temperatures 20–100 °C. We find that the effective gas-molecule collision diameter  $d_g$  decreases with T in both gases, which can be attributed to an enhanced surface *penetration* between both colliding entities with an increasingly energetic impact. The clear, monotonic increase in the value of the polarization correction parameter  $\beta$  with T indicates that the dynamics of IL nanodrop–gas molecule scattering are temperature dependent. A weaker temperaturedependent behavior is also observed for the drag enhancement factor  $\xi$ , with experimental values remaining always within less than 5% of Millikan's for all drift gas-temperature conditions examined.

We end by noting that the availability of values for the parameters  $d_g$ ,  $\beta$ , and  $\xi$  enable determining true (i.e., geometric) cross-sections of globular ions from electrical mobility measurements in molecular gases. A number of specialists in IMS-based determination of molecular structures have advocated the exclusive use of He as drift gas for three important reasons, namely (i) its small polarizability, leading to a negligible z-dependence of the cross-section, (ii) its minimal tendency to form adsorbate layers on the target molecule, which would modify artificially its cross-section and, finally, (iii) its minimal size, making the  $d_g/d$  shift relatively small. These advantages over other drift gases are serious indeed, at least as long as these three effects are not corrected. We now know, nevertheless, how to correct them accurately for globular ions in two molecular gases, air and CO<sub>2</sub>. In contrast, and in spite of its wide use, analogous empirically-determined values of the finite  $d_{\sigma}$  for He are not available. Advocates of the use of He as the most appropriate drift gas have in fact tended to report cross-sections in He as if they were a characteristic of the target ion, rather than a binary property of the ion-He pair. Our measurements enable an initial, quantitative evaluation of the real advantages of He. We have shown that the polarization correction in molecular gases is relatively small, so even an approximate correction with the kinds of ambiguities here reported make the residual (or incompletely corrected) polarization effects as negligible as those typical of He measurements. Similarly, given the high precision with which we can measure  $d_g$  in molecular gases, the ambiguity in the  $d_g$ -correction in air or CO<sub>2</sub> is negligible for all practical purposes. On the other hand, the  $d_g$  correction in He is by no means negligible. The Lennard-Jones diameter of He is comparable to our measured  $d_g$  in air, but will surely differ substantially from  $d_{g,He}$ . The error of a  $d_g$ -uncorrected cross-section in He is thus surely far larger than that of a  $d_{g}$ corrected cross section in air. As an example, for a globule 2 nm in diameter, an uncertainty of just 0.5 Å in  $d_{g,He}$  would result in a 5% uncertainty in the cross-section, considerably larger than the associated error in our corrected cross-section in air or CO<sub>2</sub>. These considerations therefore suggest that the potential advantage of He over air /  $N_2$  or  $CO_2$  will not be realized in practice until  $d_g$  values are measured for He. Even then, the approach here proposed will yield corrected, true cross-sections essentially indistinguishable in air  $/ N_2$ , CO<sub>2</sub>, and He.

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