A MODEL CALCULATION OF TRANSPORT COEFFICIENT
FOR SMALL NEGATIVE IONS IN THE TROPOSPHERE

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Abstract. Drift velocities and diffusion coefficients of 30 small tropospheric negative ions are calculated by collision integrals using the (exp,4) core potential at altitudes of 0.0km, 5.0km, and 10.0km. The ions are classified into three groups; NO_3^- ion clusters, HSO_4^- ion clusters, and some negative hydrocarbons. Five sets of two potential parameters, the steepness and the normalized rigid core radius, are employed for these ion/air combinations. Calculated mobilities of NO_2^- and $\text{NO}_3^- \cdot (\text{H}_2\text{O})_n$ ($n=0,1,2$) are compared with their experimental values, and we find that the agreement is excellent. Based upon the theory of dynamic equilibrium of reactive ion transport, a pair of formulae to determine the ion/molecule reaction rate of tropospheric negative ions is proposed and applied for the analysis of $\text{HSO}_4^- \cdot (\text{HNO}_3)_n$ ion-cluster family ($n=1,2$).

1. Introduction

In situ observation of ion compositions in the troposphere by modern mass spectrometry has revealed the presence of two major negative ion cores, NO_3^- and HSO_4^- , and their ion cluster families (Heitmann and Arnold, 1983; Eisele, 1989). These ion clusters, which are produced by ion/molecule association reactions, are, in general, composed of the ion core and several H_2O , HNO_3 , and H_2SO_4 molecules. The rate of these reactions is mainly controlled by mean relative translational energy between an ion and those trace amount of atmospheric molecules. The ions gain the energy from the electric field generated in the troposphere (Wählin, 1994). Therefore, the transport coefficient (drift velocity and diffusion coefficient) of ions has a position as a fundamentally important quantity for elucidating the tropospheric ion chemistry. However, for most of the large negative ion clusters, no transport data is available at present both experimentally and theoretically. Experimental difficulty in Ion Mobility Spectrometry (IMS) may arise from their extremely small bond dissociation energies (for example, Radzig and Smirnov, 1985). From theoretical standpoint, no appropriate and versatile interaction potential model between an ion cluster and an (effective) air molecule has been established for the calculation of collision integrals (Mason and McDaniel, pp.226-229, 1988).

Recently, we have developed an (exp,4) core potential model (Iinuma and Nishikatsu, 1997) to calculate the drift velocities and diffusion coefficients of 30 positive ions, which have been identified in the troposphere during the last decade. Comparing those with some experimental transport data, this potential has been proved to be useful for small ion cluster/air molecule combinations. Based upon the same numerical method, we calculate the drift velocities and diffusion coefficients of 30 tropospheric negative ions. The present paper reports them at altitudes of 0.0 km, 5.0km, and 10.0km. Also, it is shown that those transport coefficients enable us to derive the rates of ion/molecule reactions by making use of dynamic equilibrium condition, which probably governs the tropo-

spheric ion chemistry (Iinuma et al., 1993).

2. Theoretical model

Present method of numerical calculation to obtain drift velocity and diffusion coefficient of ions has been precisely reported in the previous paper (Iinuma and Nishikatsu, 1997), and will be only outlined here.

The potential model proposed as a function of separation distance r is represented by

$$\left\{ \begin{array}{ll} V(r) = \frac{4\epsilon}{k-4} \left[\exp\left(\frac{k(r_m-r)}{r_m-a}\right) - \frac{k}{4} \left(\frac{r_m-a}{r-a}\right)^4 \right] & r \geq r_{\max} \\ V(r) = \infty & r < r_{\max} \end{array} \right. \quad (1)$$

where ϵ is the depth of potential minimum, r_m is the position of the potential minimum, and k (>4) and a^* ($=a/r_m$; $1 \geq a^* \geq 0$) are its steepness factor and the normalized rigid core radius, respectively. The $r_{\max}$ is the value of r at a spurious maximum of $V(r)$. Then, the true reduced core radius of $V(r)$, b^* , is defined by $b^* = r_{\max}/r_m$. This potential model consists of a repulsive term of exponential type and an attractive term of r^{-4} type, including a rigid core radius in it. For physicochemical study of gaseous ions presented in the atmospheric environment, this model appears to be more realistic than the Lennard-Jones potential as well as its some modified versions such as Buckingham-Corner potential (Hirschfelder et al., 1964) etc.

The reduced collision integral Ω^* as a function of reduced effective temperature T_{eff}^* (Mason and McDaniel, pp.226-229, 1988; Iinuma and Nishikatsu, 1997) can be calculated from this potential by numerical integration method. The reduced mobility (the value reduced to S.T.P. condition) of singly charged ion in air is expressed in terms of Ω^* as

$$K_0 = \frac{5.469 \times 10^{-3}}{(\epsilon r_m^4 M_{\text{IM}} T_{\text{eff}}^*)^{1/2} \cdot \Omega^*(T_{\text{eff}}^*)} \quad (2)$$

where M_{IM} is the reduced mass of an ion and an effective air molecule ($=28.97\text{amu}$; Warneck, 1988). The units employed are K_0 in $\text{m}^2\text{V}^{-1}\text{s}^{-1}$, ϵ in eV, r_m in Å, M_{IM} in amu, and both T_{eff}^* and Ω^* are dimensionless quantity. Making use of the K_0 in Eq. (2) and the Nernst-Townsend-Einstein relation (Mason and McDaniel, pp.138-139, 1988), the drift velocity U and the diffusion coefficient D are represented as

$$U = 2.6868 \times 10^4 \cdot K_0 \cdot E / N \quad (3)$$

$$D = 2.3153 \times 10^{21} \cdot K_0 \cdot T / N \quad (4)$$

where E , N , and T are the electric field strength, the air number density, and the air temperature, respectively. The units are U in ms^{-1} , D in m^2s^{-1} , T in degrees Kelvin, and N in m^{-3} , while the ratio E/N in Eq. (3) employs the units of "Townsend" ($1\text{Td}=10^{-21}\text{Vm}^2$). The value of E/N can be obtained from the theory of atmospheric electricity developed by Wählén (1994) and the data of U. S. Standard Atmosphere (Warneck, 1988).

3. Results and discussion

The values of N , T , and E/N employed for the present calculations are listed in Table 1. Five sets of (k , a^*) combinations in Eq. (1) are determined appropriately for 30 negative ions; (17, 0.07), (16, 0.12), (16, 0.15), (15, 0.18), and (14, 0.20), by taking into account the differences of their molecular weight and their chemical forms. The corresponding values of b^* are 0.10531, 0.16175, 0.19033, 0.22881, and 0.26002, respectively.

Table 1. Number density and temperature of air, and E/N at 0.0km, 5.0km, and 10.0km. The values of E/N are obtained from Wählén's theory (Wählén, 1994).

	$N(\text{m}^{-3})$	$T(\text{K})$	$E/N(\text{Td})$
0.0km	2.55×10^{25}	288.15	5.0×10^{-3}
5.0km	1.54×10^{25}	255.68	1.1×10^{-3}
10.0km	8.60×10^{24}	223.25	6.0×10^{-4}

The calculated mobilities of ions are listed in Table 2, together with their molecular weight, the potential parameters, and the experimental values presently available.

According to the IMS experiment carried out by Hõrrik et al. (1994), most of the mobility values of negative ions in air are concentrated in the interval of 0.6×10^{-4} and $2.5 \times 10^{-4} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$. The present values are put in this interval except for NO_2^- . In fact, the NO_2^- is a daughter (or fragmented) ion observed by the collisional dissociation experiment of tropospheric NO_3^- ion (Eisele, 1989). So, only this membership may be rather irrelevant.

The drift velocities U and diffusion coefficients D at altitudes of 0.0 km, 5.0km, and 10.0km are listed in Table 3. These are calculated from Eqs. (3) and (4) using the mobility values listed in Table 2. We find in Table 3 that the overall tendency of U and D in molecular weight as well as in altitude appears to be the same as that of the positive ions (Iinuma and Nishikatsu, 1997). The only difference is that the mean values both of U and D for negative ions are a little smaller than those of positive

Table 2. Calculated and experimental reduced mobilities of negative ions in the troposphere.

Ions	MW	(k, a [†])	ε (meV)	r _m (Å)	K ₀ (×10 ⁻⁴ m ² V ⁻¹ s ⁻¹)	
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NO ₂ ⁻	46	(17, 0.07)	75.0	3.7	2.60 a)	2.58
C ₂ H ₃ O ₂ ⁻	59	(16, 0.15)	37.1	4.9		2.26
NO ₃ ⁻	62	(16, 0.12)	38.1	4.7	2.37 a)	2.38
NO ₃ ⁻ · H ₂ O	80	"	32.3	4.9		2.32
CH ₃ SO ₃ ⁻	95	(16, 0.15)	29.2	5.2		2.14
HSO ₄ ⁻	97	(16, 0.12)	35.0	4.8		2.26
C ₃ H ₃ O ₄ ⁻	103	(16, 0.15)	23.3	5.5		2.12
NO ₃ ⁻ · HNO ₃	125	"	17.6	5.9	2.05 a)	2.05
NO ₂ · SO ₄ ⁻	142	"	16.5	6.0		2.02
NO ₃ ⁻ · HNO ₃ · H ₂ O	143	"	14.5	6.2		1.99
(NO ₃ · HSO ₃) ⁻	143	"	15.4	6.1		2.00
HSO ₄ ⁻ · HNO ₃	160	"	13.6	6.3		1.95
NO ₃ ⁻ · HNO ₃ · (H ₂ O) ₂	161	"	12.0	6.5		1.91
NO ₃ ⁻ · HNO ₃ · HCl	161.5	"	12.7	6.4		1.93
C ₃ H ₃ O ₄ ⁻ · HNO ₃	166	(15, 0.18)	15.1	6.4		1.82
NO ₃ ⁻ · (HNO ₃) ₂	188	"	14.2	6.5	1.79 a)	1.79
HSO ₄ ⁻ · H ₂ SO ₄	195	"	15.1	6.4		1.80
NO ₃ ⁻ · (HNO ₃) ₂ · H ₂ O	206	"	13.4	6.6		1.76
HSO ₄ ⁻ · HSO ₅	210	"	14.2	6.5		1.76
HSO ₄ ⁻ · H ₂ SO ₄ · H ₂ O	213	"	11.9	6.8		1.72
HSO ₄ ⁻ · (HNO ₃) ₂	223	"	10.6	7.0		1.68
HSO ₄ ⁻ · (HNO ₃) ₂ · H ₂ O	241	(14, 0.20)	10.9	7.2		1.58
HSO ₄ ⁻ · HSO ₃ · HNO ₃	241	"	11.5	7.1		1.59
NO ₃ ⁻ · (HNO ₃) ₃	251	"	10.9	7.2		1.58
NO ₃ ⁻ · (HNO ₃) ₃ · H ₂ O	269	"	10.3	7.3		1.56
HSO ₄ ⁻ · HSO ₅ · HNO ₃	273	"	9.2	7.5		1.52
HSO ₄ ⁻ · H ₂ SO ₄ · HNO ₃ · H ₂ O	276	"	8.7	7.6		1.50
HSO ₄ ⁻ · (HNO ₃) ₃	286	"	8.7	7.6		1.50
HSO ₄ ⁻ · (H ₂ SO ₄) ₂	293	"	7.9	7.8		1.46
HSO ₄ ⁻ · (H ₂ SO ₄) ₂ · HNO ₃	356	"	7.5	7.9		1.43

a) Böhringer et al., 1987

Table 3. Calculated drift velocities U and diffusion coefficients D of tropospheric negative ions at three different altitudes. U and D are expressed in the units of 10^{-2}ms^{-1} and $10^{-4}\text{m}^2\text{s}^{-1}$, respectively.

Ions	MW	alt. =0. 0km		alt. =5. 0km		alt. =10. 0km	
		U	D	U	D	U	D
NO_2^-	46	3. 47	0. 067	0. 76	0. 099	0. 42	0. 155
$\text{C}_2\text{H}_3\text{O}_2^-$	59	3. 04	0. 059	0. 67	0. 087	0. 36	0. 136
NO_3^-	62	3. 20	0. 062	0. 70	0. 091	0. 38	0. 143
$\text{NO}_3^- \cdot \text{H}_2\text{O}$	80	3. 12	0. 061	0. 69	0. 089	0. 37	0. 139
CH_3SO_3^-	95	2. 87	0. 056	0. 63	0. 082	0. 34	0. 129
HSO_4^-	97	3. 04	0. 059	0. 67	0. 087	0. 36	0. 136
$\text{C}_3\text{H}_3\text{O}_4^-$	103	2. 85	0. 055	0. 63	0. 081	0. 34	0. 127
$\text{NO}_3^- \cdot \text{HNO}_3$	125	2. 75	0. 054	0. 61	0. 079	0. 33	0. 123
$\text{NO}_2^- \cdot \text{SO}_4^-$	142	2. 71	0. 053	0. 60	0. 078	0. 33	0. 121
$\text{NO}_3^- \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$	143	2. 67	0. 052	0. 59	0. 076	0. 32	0. 120
$(\text{NO}_3^- \cdot \text{HSO}_3^-)$	143	2. 69	0. 052	0. 59	0. 077	0. 32	0. 120
$\text{HSO}_4^- \cdot \text{HNO}_3$	160	2. 62	0. 051	0. 58	0. 075	0. 31	0. 117
$\text{NO}_3^- \cdot \text{HNO}_3 \cdot (\text{H}_2\text{O})_2$	161	2. 57	0. 050	0. 56	0. 073	0. 31	0. 115
$\text{NO}_3^- \cdot \text{HNO}_3 \cdot \text{HCl}$	161. 5	2. 59	0. 050	0. 57	0. 074	0. 31	0. 116
$\text{C}_3\text{H}_3\text{O}_4^- \cdot \text{HNO}_3$	166	2. 44	0. 048	0. 54	0. 070	0. 29	0. 109
$\text{NO}_3^- \cdot (\text{HNO}_3)_2$	188	2. 40	0. 047	0. 53	0. 069	0. 29	0. 108
$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4$	195	2. 42	0. 047	0. 53	0. 069	0. 29	0. 108
$\text{NO}_3^- \cdot (\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$	206	2. 36	0. 046	0. 52	0. 068	0. 28	0. 106
$\text{HSO}_4^- \cdot \text{HSO}_5$	210	2. 36	0. 046	0. 52	0. 068	0. 28	0. 106
$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	213	2. 31	0. 045	0. 51	0. 066	0. 28	0. 103
$\text{HSO}_4^- \cdot (\text{HNO}_3)_2$	223	2. 26	0. 044	0. 50	0. 065	0. 27	0. 101
$\text{HSO}_4^- \cdot (\text{HNO}_3)_2 \cdot \text{H}_2\text{O}$	241	2. 12	0. 041	0. 47	0. 061	0. 25	0. 095
$\text{HSO}_4^- \cdot \text{HSO}_3 \cdot \text{HNO}_3$	241	2. 14	0. 042	0. 47	0. 061	0. 26	0. 096
$\text{NO}_3^- \cdot (\text{HNO}_3)_3$	251	2. 12	0. 041	0. 47	0. 061	0. 25	0. 095
$\text{NO}_3^- \cdot (\text{HNO}_3)_3 \cdot \text{H}_2\text{O}$	269	2. 10	0. 041	0. 46	0. 060	0. 25	0. 094
$\text{HSO}_4^- \cdot \text{HSO}_5 \cdot \text{HNO}_3$	273	2. 04	0. 040	0. 45	0. 058	0. 25	0. 091
$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$	276	2. 01	0. 039	0. 44	0. 058	0. 24	0. 090
$\text{HSO}_4^- \cdot (\text{HNO}_3)_3$	286	2. 01	0. 039	0. 44	0. 058	0. 24	0. 090
$\text{HSO}_4^- \cdot (\text{H}_2\text{SO}_4)_2$	293	1. 96	0. 038	0. 43	0. 056	0. 24	0. 088
$\text{HSO}_4^- \cdot (\text{H}_2\text{SO}_4)_2 \cdot \text{HNO}_3$	356	1. 92	0. 037	0. 42	0. 055	0. 23	0. 086

ions. This indicates that the mean molecular weight of the negative ions identified so far is much heavier than the positive ions. It is commonly known, however, that the mean drift velocity of positive ions is lower than the negative ions in the atmosphere (Hörrik et al., 1994; Knudsen and Israelsson, 1994). This contradiction suggests that a large number of much heavier positive ion clusters and aerosol particles, which are not yet precisely identified, are still present. The molecular weight of those ions may exceed far more than 500 amu.

Finally, we derive a pair of useful formulae to obtain the forward and the reverse reaction rate of clustering reactions in dynamic equilibrium (Iinuma et al., 1993). In dynamic equilibrium, all the ionic species reaches a stable state because of the dynamic balance between their transport processes and all ion/molecule reactions occurring in the system. However, every ion is still drifting, diffusing, and reacting with ambient molecules under the influence of outer electric field.

When two ionic species X and Y satisfy this balance condition, an equilibrium of forward and reverse reaction is attainable;

where k_f and k_r are the forward and the reverse reaction rate. To obtain the transport coefficients and reaction rate constants of X and Y, we can resort to the solution of coupled diffusion-reaction equations for multiple ion swarms. If no reaction of Eq.(5) occurs, X and Y are simply drifting and diffusing independently so that we must observe two separated pure Gaussian-type arrival time spectra (ATS). However, when the reactive ion transport attains a dynamic balance, the profile of their ATS will change markedly. Figure 1 shows it; the both spectra (two solid curves: X and Y) appear to be almost same Gaussian profile with the same peak position (around β) and the same FWHM γ , except for their spectrum area (a slight difference of two peak positions δ in Fig.1 is neglected at present, while the difference is essentially important for precise determination of the transport coefficients and reaction rates: Iinuma et al., 1994). We now focus on the X+Y spectrum (the dashed curve: the sum of X and Y), which also displays the same Gaussian profile with the same peak position β , and the same FWHM γ . According to the dynamic equilibrium theory (Iinuma et al., 1994), the X+Y spectrum is represented by the mean drift velocity U_e and the mean diffusion coefficient D_e ;

$$U_e = \frac{k_r U_1 + k_f U_2}{k_f + k_r} \quad (6)$$

$$D_e = \frac{k_r D_1 + k_f D_2}{k_f + k_r} + \frac{k_f k_r (U_1 - U_2)^2}{(k_f + k_r)^3} \quad (7)$$

where U_1 and U_2 are the drift velocities of X and Y, and D_1 and D_2

are their diffusion coefficients. It is noted that U_e and D_e are measurable in drift-tube experiment without mass spectrometer, because these two values can simply be determined from β and γ of the X+Y ATS using

Fig. 1. Arrival time spectra of X and Y in dynamic equilibrium, which are numerically obtained from the solution of coupled diffusion-reaction equations for two ionic species (two solid curves). A dashed curve is the ATS produced by adding X and Y at the same elapsed time. β , the peak position of X+Y spectrum: γ , the FWHM of all spectra: δ , the peak difference between X and Y: ϵ , the area ratio of X and Y.

the drift distance employed in the measurement. Then, Eqs (6) and (7) allow for us to derive k_f and k_r as

$$k_f = \frac{A_1^2 \cdot A_4}{(1 + A_1)^2 (A_2 + A_1 \cdot A_3)} \quad (8)$$

$$k_r = \frac{A_1 \cdot A_4}{(1 + A_1)^2 (A_2 + A_1 \cdot A_3)} \quad (9)$$

where

$$\left\{ \begin{array}{ll} A_1 = \frac{U_1 - U_e}{U_e - U_2} , & A_2 = \frac{D_e - D_1}{D_e} \\ A_3 = \frac{D_e - D_2}{D_e} , & A_4 = \frac{(U_1 - U_2)^2}{D_e} \end{array} \right. \quad (10)$$

The values U_1 , U_2 , D_1 , and D_2 may be available in Table 3.

Although the accurate determination of U_e and D_e by drift-tube experiments appears, in general, to be rather formidable, the following precaution and an additional measurement technique may be helpful; (1) Check the form of the measured ATS which should attain a Gaussian-type profile. (2) To confirm the ionic species constituting the ATS, it is much better to identify the presented ions using mass spectrometry.

To the best of our knowledge, however, no experimental ATS data appropriate for present analysis are available so far. We therefore test the soundness of Eqs. (8)-(10) by employing a hypothetical data set of $\text{HSO}_4^- \cdot \text{HNO}_3$ and $\text{HSO}_4^- \cdot (\text{HNO}_3)_2$ ion clusters at the ground level:

According to a model of tropospheric negative ion chemistry developed by Kawamoto and Ogawa (1986), the $\text{HSO}_4^- \cdot (\text{HNO}_3)_n$ ion-cluster family is originated only from the forward reaction of $\text{NO}_3^- \cdot (\text{HNO}_3)_n$ family with a H_2SO_4 molecule. This scheme suggests that a series of $\text{HSO}_4^- \cdot (\text{HNO}_3)_n$ ions constitutes one terminal-ion-family, which appears to be much more stable chemically than other negative ion clusters in the troposphere.

In Table 3, we find the drift velocities and diffusion coefficients of $\text{HSO}_4^- \cdot \text{HNO}_3$ (suffix No.1) and $\text{HSO}_4^- \cdot (\text{HNO}_3)_2$ (suffix No.2); $U_1 = 2.62 \times 10^{-2} \text{ ms}^{-1}$, $U_2 = 2.26 \times 10^{-2} \text{ ms}^{-1}$, $D_1 = 5.1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, and $D_2 = 4.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. In the equilibrium attained by Eq. (11), it is possible to measure the ATS, which will display a Gaussian profile like the dashed ATS in Fig.1. From its β and γ we can determine the values of U_e and D_e , for example, to be $2.277 \times 10^{-2} \text{ ms}^{-1}$ and $4.433 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. Making use of these values, Eqs. (8)-(10) result $k_f = 3640 \text{ s}^{-1}$ and $k_r = 180 \text{ s}^{-1}$. The corresponding values cited commonly in atmospheric chemistry are 2600 s^{-1} and 130 s^{-1} , respectively (for example, Kawamoto and Ogawa, 1986). Natural concentrations of HNO_3 and air $[\text{M}]$ in Eq. (11) employed are $1.0 \times 10^{16} \text{ m}^{-3}$ and $2.55 \times 10^{25} \text{ m}^{-3}$, respectively (Luts and Salm, 1994). Again, it should be emphasized that this analysis is based upon a hypothetical data set of U_e and D_e , but the general soundness of Eqs. (8)-(10) has been justified.

4. Conclusions

The drift velocities and diffusion coefficients of 30 tropospheric negative ions are calculated at three different altitudes. Their overall

tendency in molecular weight as well as in altitude is the same as that of positive ions. However, their mean values are a little smaller than positive-ion group. By employing dynamic equilibrium condition in the troposphere, the forward and reverse reaction rates of $\text{HSO}_4^- \cdot (\text{HNO}_3)_n$ ($n=1, 2$) are estimated from their drift velocities and diffusion coefficients.

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