Vibrational Temperature of $O_2{}^+$ and $N_2{}^+$ Drifting at Elevated E/N in Helium

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The vibrational temperature, T_v, of $N_2{}^+$ and $O_2{}^+$ ions drifting in a helium buffer has been determined for the first time quantitatively as a function of E/N. For both ions T_v reaches ~ 3000 K at $E/N \simeq 150 \times 10^{17}$ $\mathrm{V \cdot cm^2}$. This result resolves various previously inexplicable aspects of the behavior of ion-neutral reactions as a function of energy.

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According to Wannier,[1] the mean kinetic energy K_i of ions drifting in a buffer gas is governed by the relation

$$K_i = \tfrac{3}{2} k_B T_g + \tfrac{1}{2}(M_B + M_i) v_d^2 \tag{1}$$

where k_B is the Boltzmann constant, T_g the buffer-gas temperature, M_B and M_i the masses of the buffer gas and ions, respectively, and v_d the drift velocity of the ions. Thus the mean relative kinetic energy between ions and reactants (dispersed in the buffer gas and having a mass M_R) in the center-of-mass frame is[2]

$$K_{\mathrm{c.m.}} = \tfrac{3}{2} k_B T_g + \tfrac{1}{2} M_R v_d^2 \left(\frac{M_i + M_B}{M_i + M_R} \right). \tag{2}$$

In drift experiments the energy dependence of reaction rate constants can be obtained by varying the value of E/N (E representing the electric field strength and N the buffer-gas number density), causing a variation in v_d, according to[3]

$$v_d = \mu E,$$

where μ is the ion mobility.

Many rate coefficients of reactions between molecular ions and neutrals differ greatly in their dependence on $K_{\mathrm{c.m.}}$ when the investigations are performed in buffer gases of different masses.[4-12] These variations have been attributed to differences in vibrational excitation of the ions in collisions with specific buffer gases. If a given ion-neutral pair is to have the same center-of-mass energy in different buffer gases, E/N and thus v_d will be quite different in the two cases. Since the ion–buffer-gas collisions govern the vibrational excitation of the ion, different effective vibrational temperatures exist for the same ion at a given $K_{\mathrm{c.m.}}$ in different buffer gases. This is reflected in different rate coefficients in the respective buffer gases whenever internal excitation promotes or inhibits a reaction.

The collision energy between ions and the buffer gas usually is higher in heavy buffer gases, such as Ar or Ne, than in He. A consequence of this is a higher internal excitation of molecular ions in the heavier buffer gases. Experimentally, the presence of ionic internal excitation with Ar as buffer gas was demonstrated[6] by adding traces of the parent gas P ($P = O_2$, CO_2) of the ions P^+ to the Ar buffer in the reaction region of a flow-drift tube. As a result of the fast-quenching reaction,

$$P^+(v > 0) + P \rightarrow P + P^+(v = 0), \tag{3}$$

the vibrational temperature of P^+ ions was thus lowered drastically and as expected, the rate coefficients measured with P added to the Ar buffer gas were shifted towards the rate coefficients obtained in the light He buffer gas. The same addition of P to the He buffer gas, however, did not show any significant shift in the rate coefficients, hence the general assumption in literature of recent years[5-12] that He does not excite internal vibrations of molecular ions, even at high E/N. Therefore it was assumed that the dependences of rate coefficients on $K_{\mathrm{c.m.}}$ [according to Eq. (2)] would reflect the "pure" kinetic energy dependences, without any influence due to internal excitation of the ions, while the dependences of the rate coefficients for the same reactions obtained in heavier buffers, such as Ar, Ne, or N_2 would show the influence of kinetic plus internal energy.

In contrast to that, theoretical calculations of Viehland and co-workers[13-16] predict that molecular ions drifting in any atomic buffer gas (including He) will reach an effective internal temperature T_{eff} given by

$$\tfrac{3}{2} k_B T_{\mathrm{eff}} [+ (M_B/M_i)\xi] (\tfrac{3}{2} k_B T + \tfrac{1}{2} M v_d^2)(1 + \beta), \tag{4}$$

where ξ is a dimensionless ratio of collision integrals that characterizes the fractional energy loss due to inelastic collisions, and β is a minor correction term (in the range of a very few times 10^{-2}). Values of ξ for ions drifting in N_2 have been obtained recently by Viehland and Fahey[17] by comparing ion mobilities obtained as a function of E/N and as a function of the temperature of the buffer gas. Equation (4) also predicts a considerable increase of the internal temperature of molecular ions in a He buffer, unless ξ would have an extremely peculiar dependence on E/N.

In the present work we have investigated the vibrational temperature of $N_2{}^+$ and $O_2{}^+$ ions drifting in He in the following way. Mass selected, vibrationally relaxed ions (and for test purposes highly excited ions, as mentioned later) are injected into a fast-flow drift tube, the drift region of which is divided into two sections as shown in the schematic drawing of Fig. 1.[18] In section A the value E/N is variable, while in section B *no field is applied.* If ions traveling through section A under elevated E/N become vibrationally excited they keep their excitation nearly unchanged on the way through the field-free section B, because He has proven to be quite inefficient in quenching vibrational excitation *under zero-field conditions.*[12,19–23] *Quenching rate* coefficients $k_q \leq 5\times10^{-13}$ cm^3 sec^{-1} at $E/N=0$ for molecular ions such as O_2^+ and N_2^+, having vibrational spacings which are large in comparison with kT (O_2^+, $\omega_e=1876.4$ cm^{-1}; N_2^+, $\omega_e=2207.2$ cm^{-1}), can be inferred from the data in Refs. 9, 12, and 19.

Adding a monitor gas through the inlet at section B, which undergoes reactions with $R^+(v>0)$, but not with $R^+(v=0)$, where $R=N_2$ or O_2, allows us to determine the fraction of excited $R^+(v>0)$ ions resulting from the collisional heating in section A at various values of E/N. In the case of N_2^+, Ar is used as a monitor, which converts $N_2^+(X,v\geqslant1)$ into Ar^+ in a fast charge transfer ($k\simeq5\times10^{-10}$ cm^3 sec^{-1}),[19,20] while the reaction of $N_2^+(X,v=0)$ with Ar is extremely slow ($k=1.7\times10^{-13}$ cm^3 sec^{-1}). Typical declines of the N_2^+ ion signal (monitored in the ion detection system) are observed when monitor-gas Ar is added to section B, as shown in Fig. 2., the decline of the N_2^+ signal being matched by an increase of the Ar^+ signal. The ratio $a/b=\alpha$ thus is equal to the ratio $N_2^+(X,v\geqslant1)/N_2^+(X,v\geqslant0)=\alpha$ which is connected to the vibrational temperature of the ions, $T_v=T_{\rm eff}$ by the following relation:

$$N_2^+(X,v\geqslant1)/N_2^+(X,v\geqslant0)=\sum_{v=1}^{v_{\rm diss}}\exp(-\Delta E_n/k_{\rm B}T_v)\Big/\sum_{v=0}^{v_{\rm diss}}\exp(-\Delta E_n/k_{\rm B}T_v)=\alpha, \tag{5}$$

where ΔE_n denotes the vibrational spacing, $\Delta E_n=E_n-E_0$.[24] The results for T_v obtained in this way from the measured values α in the regime $0\leqslant E/N\leqslant160$ Td [1 Td (townsend) $=10^{17}$ V·cm^2] are shown in Fig. 3 as well as vibrational temperatures for O_2^+. These values have been obtained using CH_4 as a monitor, making use of recent data of Durup-Ferguson *et al.*,[12] showing that $O_2^+(X,v\geqslant2)$ reacts rapidly with CH_4 ($k=1.7\times10^{-10}$ cm^3 sec^{-1}) according to

$$\begin{array}{llr} O_2^+(X,v\geqslant2)+CH_4\to CH_3{}^+HO_2 & 37\% & \\ \qquad\qquad\qquad\qquad\to CH_4{}^+ + O_2 & 52\% & \\ \qquad\qquad\qquad\qquad\to CH_3O_2{}^+ + H & 11\% & (6) \end{array}$$

while $O_2^+(X,v=1)$ is quenched by

$$O_2^+(X,v=1)+CH_4\to O_2^+(X,v=0)+CH_4 \tag{7}$$

with a rate $k_q\simeq6\times10^{-10}$ cm^3 sec^{-1}. $O_2^+(X,v=0)$ reacts only very slowly ($k\simeq6\times10^{-12}$ cm^3 sec^{-1}) with CH_4, thus the decline of the O_2^+ signal due to this reaction is negligible as long as only a moderate amount of CH_4 monitor gas is used. The results summarized in Fig. 3 show that T_v for N_2^+ and O_2^+ reaches about 3000 K at E/N values of ~150 Td, i.e., up to ~30% of the ions are vibrationally excited.

Additional checks were made in two ways: (a) Excited N_2^+ ions, $N_2^+(X,v\geqslant1)/N_2^+(X,v\geqslant0)>0.4$, were injected into the drift tube and their "cooling" as dependent on E/N was observed by varying E/N in section A and measuring at the same time the ratio $\alpha=N_2^+(X,v\geqslant1)/N_2^+(X,v\geqslant0)$ in section B by adding Ar monitor gas as described above. (b) With E/N kept constant, the length L of section A was changed and α was measured as a function of L. The results can be summarized as follows:

(1) The rate coefficients for vibrational heating and

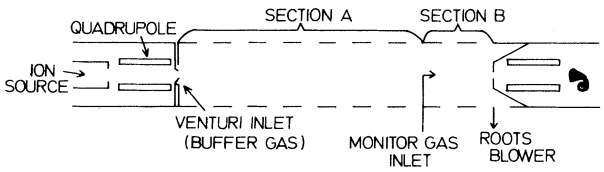

FIG. 1. Schematic drawing of the flow drift tube with selected ion injection system. In section A, E/N is variable from 0 to about 200 Td, while in section B $E/N=0$ during all the measurements performed in this investigation.

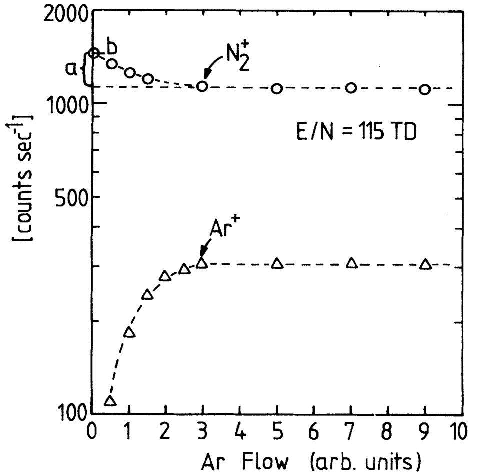

FIG. 2. Typical ion count rates for N_2^+ and Ar^+ as a function of the flow of monitor gas Ar added to section B of the drift region. [1 Td (townsend) $=10^{12}$ V·cm^2.]

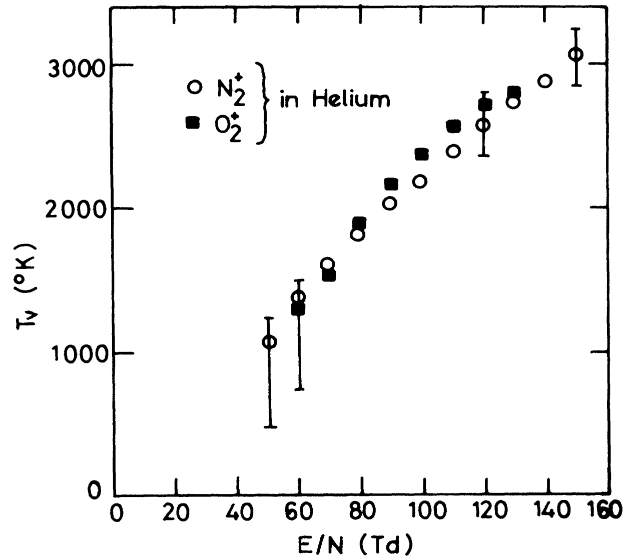

FIG. 3. Vibrational temperature of $N_2{}^+$ and $O_2{}^+$ drifting in helium buffer gas. The error bars refer to $N_2{}^+$ and are assumed to be similar for $O_2{}^+$. The larger error bars at low E/N result from the fact, that equilibrium is less readily established at low E/N than at high E/N ($\geqslant 90$ Td).

quenching of $N_2{}^+$ both increase dramatically with increasing E/N.

(2) At $E/N \geqslant 90$ Td and $p(\mathrm{He}) \geqslant 0.25$ Torr an "equilibrium" temperature T_v is always reached when $L \geqslant 50$ cm. At lower E/N this equilibrium is not reached in all cases; therefore the uncertainties in T_v as a function of E/N become larger towards lower E/N, as indicated in the error bases in Fig. 3. More detailed measurements are being performed.

It is obvious that in cases of reactions which are slow for nonexcited ions, but fast for vibrationally excited ones, this excitation may become the determining factor for the total reactivity of a process at elevated E/N. In fact the present data imply that the strong E/N dependence of the rate coefficient for the above mentioned reaction of $O_2{}^+$ with CH_4 as observed in He[5-8, 12] is largely due to the vibrational temperature (as shown in Fig. 3). $K_{\mathrm{c.m.}}$ is not the only determining factor.

The present data on T_v of $N_2{}^+$ solve a severe problem apparently connected with the endoergic reaction

$$N_2{}^+(X, v=0) + \mathrm{Ar} \rightarrow \mathrm{Ar}^+({}^2P_{3/2}) + N_2 - 0.18\ \mathrm{eV}. \qquad (8)$$

While a drift experiment[19] on reaction (8) shows a drastic rate increase with increasing $K_{\mathrm{c.m.}}$ even in a He buffer, low-energy beam experiments indicate that the cross section for charge transfer between $N_2{}^+(X, v=0)$ and Ar stays negligibly low compared to the ones for $N_2{}^+(X, v>0)$ up to 20-eV relative kinetic energy between the collision partners.[25-27] An estimation based on the present data shows that the increase of T_v of $N_2{}^+$ with rising E/N accounts for the whole increase in the rate of reaction (8) as a function of E/N as observed in the drift-tube experiment.[19] Thus the finding of beam experiments, that pure kinetic energy does not promote reaction (8), is consistent with rates obtained in the drift experiment.[18]

No significant changes of rate coefficients are observed in He when the parent gas of the drifting ions is added to the buffer (thus leading to the erroneous conclusion, as mentioned above, that no ionic vibrational excitation occurs in He). This may be explained partly in view of recent low-energy beam results[28] showing that collisions between $N_2{}^+(X, v=0)$ and $N_2(X, v=0)$ lead to products $N_2{}^+(X, v>0)$, thus causing internal heating of the ions when the collision energy significantly exceeds the vibrational spacing of the molecular ions. According to Eq. (2) the collision energy between typical molecular ions (such as $N_2{}^+$ and $O_2{}^+$) and their parent gases, added to the He buffer gas, is much larger than under similar conditions in heavy buffer gases (much lower v_d). Therefore vibrational heating due to collisions between molecular ions and their parent gases may well compete with quenching processes in He, whereas for low-energy collisions within a heavier buffer gas, quenching, and thus cooling of T_v dominates, even at elevated E/N.

With the present results some of the reported "energy dependences" of ion-neutral reactions find an explanation in the variation of T_v of the molecular ions involved and thus the role of pure kinetic energy in those proceeses needs to be reconsidered.

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