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Vibrational quenching of $NO^+(v)$ ions by Ar collisions

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Abstract

Quenching rate constants for $NO^+(v = 1)$ and $NO^+(v = 4)$ in collisions with Ar have been measured from near thermal energy up to 0.5 eV mean relative kinetic energy in a selected ion flow drift tube. The rate constants increase dramatically with KE_{CM} indicating that the quenching is dominated by the short range repulsive interaction. At higher energies the data fit linear Landau–Teller plots. These are the first L–T plots obtained for ion quenching by other than a He quencher. (Int J Mass Spectrom 223–224 (2003) 757–762)

Keywords: $NO^+(v)$; Ion vibrational relaxation; Selected ion flow drift tube

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1. Introduction

The first published systematic study of vibrationally excited small molecular ion quenching was for $NO^+(v)$ by 17 neutral molecules [1]. For quenching with N_2, CO, CO_2, CH_4, NH_3, H_2O, N_2O, and C_2H_4 energy transfer is relatively efficient at 300 K, occurring in greater than 1% of the collisions. The quenching is due to the attractive interaction potential, occurring via intermediate complex formation wherein vibrational predissociation competes with dissociation of the complex without vibrational quenching [2]. From three-body association rate constants, the vibrational predissociation rate can be determined which falls in the 10^9–$10^{10}\,s^{-1}$ range. Complex formation requires that an attractive potential well exists, with depth comparable to or greater than kT. For non-polar neutrals the ion-induced dipole attraction ($\sim\alpha e^2/r^4$) provides this well. For polar quenchers, the much stronger interaction leads to quenching with near unit efficiency. When complex formation is not significant, vibrational quenching can be induced at higher energies by a forced non-adiabatic process controlled by the repulsive interaction [3]. When the complex mechanism operates, the vibrational quenching rate increases with decrease in collision energy because the complex lifetime increases. It can of course happen that chemical bonding or non-bonding forces dominate the electrostatic interaction.

There is no fundamental difference in the vibrational quenching of ions and neutrals. However, because of the universal electrostatic attraction in the case of ions, efficient quenching via complex formation is the usual situation for ions and unusual for small neutrals with non-polar quenchers. When an appreciable attractive potential exists, such as hydrogen bonding or chemical bonding, then neutral molecule vibrational quenching also occurs via

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complex formation [4]. The model of vibrational quenching by a repulsive interaction described by Landau and Teller [3] has been successfully applied to neutral vibrational quenching for many years. The first L–T plot for an ion vibrational quenching was for the case of $N_2{}^+(v)$ quenching by He [5]. In L–T theory, the repulsive interaction, due to wave function overlap (Pauli principle), is satisfactorily represented by $V(r) \sim \exp(-r/\ell)$ where ℓ (range parameter) has been found to invariably be in the neighborhood of $\approx$0.2 Å, from vibrational quenching studies, molecular beam scattering studies and equation of state studies. In the case of the $N_2{}^+(v)$–He study, the range parameter obtained from the L–T plot, $\ell = 0.22$ Å, was substantiated by ab initio potential surface calculations [6]. For $HCN^+(v)$ quenching by He, ℓ was found to be 0.21 Å [7]. He is an obvious candidate to be a "repulsive" quencher by virtue of its small polarizability (0.205 Å^3). However, it is known that in addition to well depth, the anisotropy of the potential is critical [4], presumably by facilitating the conversion of collisional translational energy into rotational energy in the complex, allowing trapping. For example, while N_2 ($\alpha = 1.79$ Å^3) is an efficient quencher, Ar ($\alpha = 1.64$ Å^3) and Kr ($\alpha = 2.48$ Å^3) are not.

In the present study, the quenching rate constants of $NO^+(v = 1)$ and $NO^+(v = 4)$ are found to increase with KE_{CM} from thermal up to 0.5 eV and to fit L–T plots.

2. Experimental and results

The measurements were carried out in the Innsbruck selected ion flow drift tube (SIFDT) [8] with Ar used as the buffer gas. Injecting the ions with elevated energy E_{inj} (in the laboratory frame) into the Ar buffered drift tube produces vibrationally excited ions (Fig. 1). Application of an electric field in the reaction section of the drift tube changes the quenching collision energy, which scales as E/N, the ratio of electric field strength to buffer gas density. A monitor ion method [9] is used to probe the vibrational state distribution, before and after the quenching section. C_2H_5I was used to determine the concentration of $NO^+(v > 0)$, the reaction with $NO^+(v = 0)$ is endothermic and slow. C_2H_5Br was used to obtain the concentration of $NO^+(v \geq 4)$ [10]. The decrease of vibrationally excited ions between the entrance and exit of the reaction region gave quenching rate constants in the

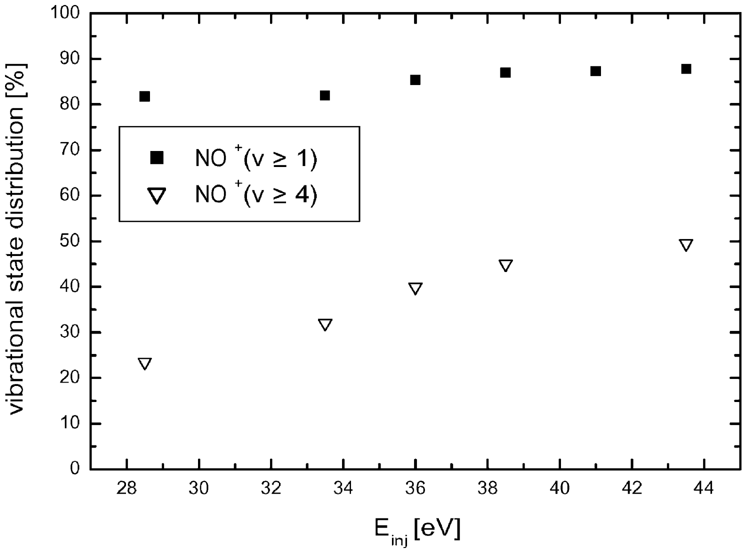

Fig. 1. Vibrational state distribution of $NO^+(v)$ ions for different injection energies E_{inj} (in the laboratory frame).

Table 1
Reduced mobilities μ_0 of NO^+ in Ar at 300 K as a function of E/N

E/N (Td)	μ_0 ($cm^2\,V^{-1}\,s^{-1}$)
35	2.4
40	2.5
50	2.5
62	2.6
70	2.7
80	2.7
92	2.8
100	2.9
110	3.0
122	3.1

E/N is the ratio of the electrostatic field strength to the Ar number density, expressed in units of $1\,\mathrm{Td} = 10^{-17}\,\mathrm{V\,cm^2}$.

usual way [11]. NO^+ mobilities in Ar were measured as a function of E/N (Table 1) in order to determine average kinetic energies in the center-of-mass frame, KE_{CM}, and to give the residence time in the quenching region. Typically, residence times, $\approx$3 ms, were short compared to radiative lifetimes τ_{rad} for $NO^+(v)$ which goes approximately as $90\,\mathrm{ms}\,v^{-1}$ [12,13]. Vibrational state distributions as a function of E_{inj} are shown in Fig. 1. The measured quenching rate constants are shown in Fig. 2. The quenching rate constant for $NO^+(v \geq 1)$ is close to the value for $NO^+(v = 1)$ since the $v = 1$ level dominates the population. Similarly the quenching rate constant for $NO^+(v \geq 4)$ is close to the value for $NO^+(v = 4)$. The quenching rate is relatively insensitive to the vibrational level distribution as seen in Fig. 3, where the initial vibrational distribution is varied by varying E_{inj} with little effect within the experimental data spread.

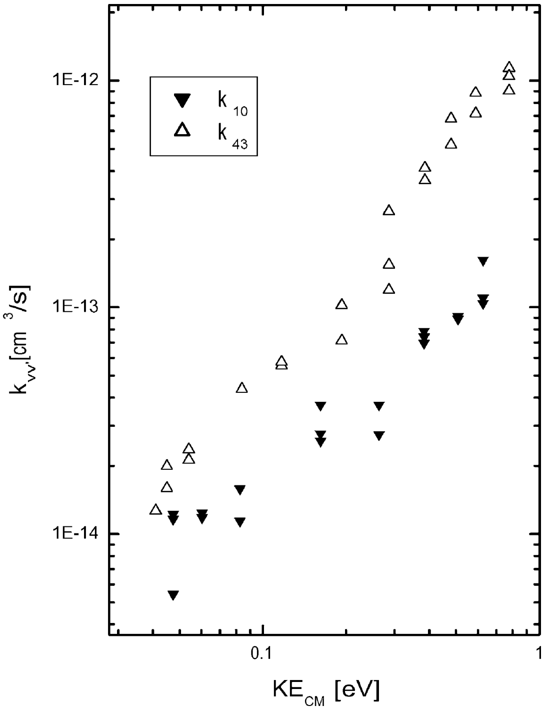

Fig. 2. Quenching rate constants k_{10} and k_{43} as a function of mean relative kinetic energy KE_{CM}.

Application of the FDT technique requires making the approximation that $KE_{CM} \approx 3/2kT$. This had been found to be valid for He buffer gas in which case ion velocity distributions are found to be approximately Maxwellian, but in the case of Ar buffer a high energy tail exists which leads to deviations from the Maxwellian velocity distribution [14,15]. Since more energetic collisions quench more efficiently this may lead to a too low value for our “effective” KE_{CM}. The L–T plots for the quenching rate constants of $NO^+(v = 1)$ and $NO^+(v = 4)$ are shown in Figs. 4 and 5. The L–T plots are linear at the highest energies and have positive deviations at lower energies. Positive deviations always occur in L–T plots at low enough energies since the contribution to the quenching by the attractive potential becomes relatively more significant.

3. Discussion

The Landau–Teller model [3] yields for the vibrational quenching rate constant

$$k_q \sim \exp\left[-\frac{3}{2}\left(\frac{\theta}{T}\right)^{1/3}\right], \quad \theta = \frac{4\pi^2\mu\ell^2\omega^2}{k_b} \qquad (1)$$

where μ is the reduced mass of the collision pair, ω the change in vibrational frequency, k_b the Boltzmann constant, T the temperature, and ℓ is the range parameter for the repulsive exponential interaction, $V(r) \sim$

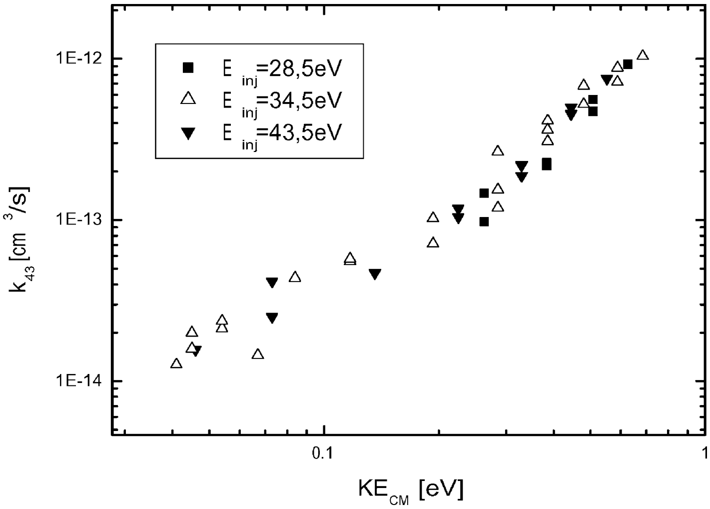

Fig. 3. Quenching rate constant k_{43} for different initial vibrational distributions.

$\exp(-r/\ell)$. ℓ has a typical value of ~0.2 Å. This has been derived in different ways and is discussed in detail by Cheng et al. [16]. L–T theory is essentially the classical expression of the adiabatic criterion for energy transfer, integrated over a Maxwellian velocity distribution. The range parameter deduced from Fig. 4 is 0.19 Å, where $k_{\geq 1 \rightarrow 0}$ is very close to k_{10}. From Fig. 5, the value of $\ell = 0.21$ Å, where $k_{\geq 4 \rightarrow k<4}$

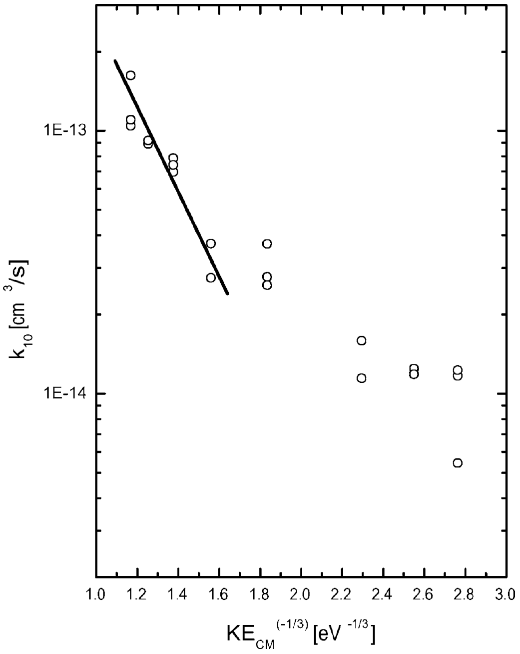

Fig. 4. Landau–Teller plot of k_{10}.

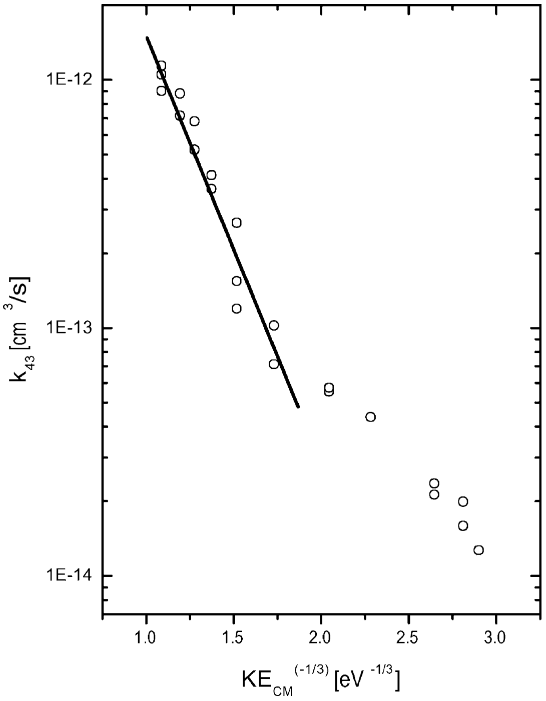

Fig. 5. Landau–Teller plot of k_{43}.

is $\approx k_{43}$. The lowest vibrational level detected by the monitor dominates higher levels. In all cases, it is clear that $\Delta v = 1$ transitions dominate since the resulting range parameters are within a reasonable range. A change of $\Delta v = 2$ would require dividing the range parameter by 2 which is unreasonable. The very deep and energetically isolated NO^+ potential surface [17] appears to lead to harmonic oscillator like behavior, i.e., a $\Delta v = 1$ propensity rule. The same selection rule ($\Delta v = 1$) was found by Wyttenbach and Bowers [18] for $NO^+(v)$ quenching with 15 neutral molecules including Ar. However, their thermal quenching rate constant for Ar ($\approx 0.4 \times 10^{-10}\,cm^3\,s^{-1}$) should be taken as an upper limit rather than an accurate value. This can be explained by the low pressure conditions in the FT-ICR experiment which cause rather high error limits for slow ($k < 10^{-10}\,cm^3\,s^{-1}$) quenching rate constants [18].

A very striking example of the transition from repulsive interaction dominated vibrational quenching at high energies to attractive potential interaction dominated at sufficiently low temperatures arises in the case of $NO^+(v)$ quenching by Ar. At room temperature the quenching is very low (Fig. 2). Hawley and Smith [19] find the quenching rate constant to equal the Langevin collision rate constant at 1 K. The rate constant for quenching will almost invariably reach very large values at extremely low temperature since the well depth due to universal Van der Waals attraction will become large enough relative to the thermal kinetic energy (i.e., kT) to allow complex formation. When the complex lifetime exceeds the vibrational predissociation lifetime (we have found this to be 10^{-9} to 10^{-10} s in several cases) then quenching will be efficient. This allows us to make the useful prediction that vibrational quenching will probably be efficient in ion temperature environments such as interstellar molecular clouds. An exception might be cases where repulsive chemical interaction overrides the electrostatic attractive interaction. An example of chemical repulsion dominating attractive interaction is the case of $NO^+(v)$ quenching by ground state $O_2(^3\Sigma)$ molecules. The very low quenching rate has been attributed to the repulsive ${NO_3}^+$ triplet entrance channel. On the other hand $NO^+(^1\Sigma, v)$ was efficiently quenched by metastable $O_2(^1\Delta_g)$ molecules. In this case, the attractive entrance channel correlates with the exothermic ${NO_3}^+$ singlet ground state [20]. However, even in such a case the longer range electrostatic potential will probably override the repulsion at even lower temperatures leading to significant vibrational quenching.

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