



ELSEVIER

International Journal of Mass Spectrometry 185/186/187 (1999) 559–563



# Vibrational relaxation of $\text{NO}^+$ ( $\nu$ ) in collisions with $\text{CH}_4$ : experimental and theoretical studies

A. Hansel<sup>a</sup>, N. Oberhofer<sup>a</sup>, W. Lindinger<sup>a,\*</sup>, V.A. Zenevich<sup>b</sup>, G.D. Billing<sup>b</sup><sup>a</sup> Institut für Ionenphysik der Universität Innsbruck, A-6020 Innsbruck, Austria<sup>b</sup> Department of Chemistry, H.C. Ørsted Institute, University of Copenhagen, DK-2100, Copenhagen, Denmark

Received 18 June 1998; accepted 12 August 1998

## Abstract

The rate constants for vibrational relaxation of  $\text{NO}^+$  ( $\nu = 1$ ) and  $\text{NO}^+$  ( $\nu = 4$ ) in collisions with  $\text{CH}_4$  were measured from thermal to 1 eV center of mass collisional energy using a selected ion flow drift tube. These experimental data are interpreted theoretically using the semiclassical (classical path) approach of Billing and the potential energy surface, constructed on the basis of the model of Gislason and Ferguson. (Int J Mass Spectrom 185/186/187 (1999) 559–563) © 1999 Elsevier Science B.V.

**Keywords:**  $\text{NO}^+$  ( $\nu$ ); Ion vibrational relaxation; Selected ion flow drift tube

## 1. Introduction

The vibrational relaxation of diatomic ions has been investigated in great detail experimentally over the last decade [1,2]. In particular, the relaxation of  $\text{NO}^+$  ( $\nu \geq 1$ ) to  $\text{NO}^+$  ( $\nu = 0$ ) in collisions with  $\text{CH}_4$  has been studied previously by Dobler et al. [3] and Morris et al. [4] at thermal energies, and by Federer et al. [5] and Richter et al. [6] in the energy regime from thermal to about 1 eV mean relative kinetic energy,  $\text{KE}_{\text{cm}}$ , between the collision partners.

In our recent studies [7,8] within the framework of the semiclassical method [9] we have undertaken an attempt to study the physical relevance of the specifically anisotropic interaction potentials resulting from the application of the postulates of the model of

Gislason and Ferguson [10]. The satisfactory results, concerning the vibrational relaxation of  $\text{O}_2^+$  and  $\text{NO}^+$  in collisions with He, obtained in these works, encouraged us to proceed with further experimental studies of similar collision systems and, theoretically, with the extension of our procedure for constructing the global interaction potentials on other vibrationally inelastic collision systems, one of which is the presently studied  $\text{NO}^+$ – $\text{CH}_4$  system.

In this article we report results on the energy dependencies of quenching rate constants  $k_{10}$  and  $k_{43}$ , respectively, for the vibrational relaxation processes



which were obtained both experimentally and theoretically within the range of mean relative collision energies  $\text{KE}_{\text{cm}}$  from thermal to about 1 eV.

\* Corresponding author.

Dedicated to the 60th birthday of Professor M.T. Bowers.

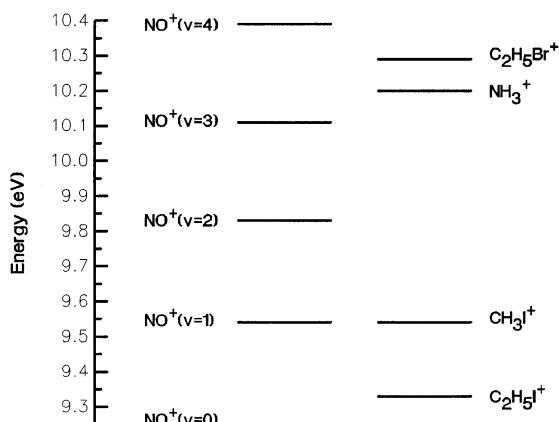


Fig. 1. Energy levels of NO<sup>+</sup> ( $v = 0 - 4$ ) and ionization energies of monitor gases used.

## 2. Experimental method

The measurements were done using the Innsbruck selected ion flow drift tube (SIFDT) apparatus, which was described elsewhere [5]. In order to obtain quenching rate constants a monitor ion method was applied which is identical to the one used by Böhringer et al. [11]. Briefly, a fixed flow of monitor gas is introduced at the monitor gas inlet just in front of the detection orifice. The resulting monitor ion signal, which is proportional to the NO<sup>+</sup> ( $v \geq n$ ) ion concentration at the monitor inlet port, is then recorded as a function of the flow of quenching gas added at the upstream reactant inlet. An exponentially decaying monitor ion signal is observed from which the quenching rate constant can be deduced in the same way as reaction rate constants are derived [12]. In Fig. 1 the energy levels NO<sup>+</sup> ( $v = 0 - 4$ ) are shown together with the ionization potentials of several monitor gases. CH<sub>3</sub>I and C<sub>2</sub>H<sub>5</sub>I can be used to determine the concentration of NO<sup>+</sup> ( $v \geq 1$ ), as NO<sup>+</sup> ( $v \geq 1$ ) performs fast charge transfer with these neutrals. NH<sub>3</sub>, and C<sub>2</sub>H<sub>5</sub>Br were used to monitor the NO<sup>+</sup> ( $v \geq 4$ ) ion concentration.

## 3. Theoretical model

The rigorous dynamical treatment of the vibrational relaxation processes investigated in this study

should take into account all vibrational and rotational degrees of freedom of CH<sub>4</sub>. But in the absence of an accurate interaction potential the use of such complicated and computer time consuming dynamical methods for the interpretation of the present experimental data would be hardly meaningful. Thus, both the procedure for the construction of the global potential energy surface (PES) and the dynamical model, we use in this study, are of approximate nature: Analyzing the vibrational relaxation of NO<sup>+</sup> ( $v$ ) in collisions with CH<sub>4</sub>, we regard CH<sub>4</sub> as a structureless particle, partially taking into account its complexity by the appropriate adjustment of the potential parameters for the corresponding effective “atom–diatom” PES.

The procedure of constructing the PES for atom–diatom systems is described in previous articles [7, 8] and briefly reviewed here. In order to obtain the whole three-dimensional (3D) PES for the AB<sup>+</sup>–M collision system (AB<sup>+</sup> = O<sub>2</sub><sup>+</sup>, NO<sup>+</sup>), based on the postulates of the model [10] of Gislason and Ferguson, we use the functional form, which was proposed earlier by Tosi et al. [13].

The essential information about the geometrical structure of O<sub>2</sub><sup>+</sup>–M and NO<sup>+</sup>–M complexes is already quantitatively estimated by Gislason and Ferguson [10]. Using the lowest unfilled molecular orbital highest occupied molecular orbital (LUMO)/(HOMO) arguments, they calculated the equilibrium geometry (values of geometric parameters in the subsequent equations) of the complex. Then, introducing the adjustable parameter which from the physical origin is the electronic coupling between the state O<sub>2</sub><sup>+</sup>–M (or NO<sup>+</sup>–M) and the charge-transfer state O<sub>2</sub>–M<sup>+</sup> (or NO–M<sup>+</sup>), Gislason and Ferguson estimated total bond energies  $D_0$  as well as incremental bond energy contributions  $D_i$  (due to “chemical” interaction) for a number of O<sub>2</sub>–M<sup>+</sup> and NO–M<sup>+</sup> complexes.

Postulating the equilibrium geometry of the complex in accord with [10] and centering the minima of the total and chemical interactions at this equilibrium geometry, we will also find the values of parameters  $\alpha_i$ ,  $\beta$ , and  $E$  in the subsequent equations.

The potential function is represented as

$$V(R, r, \varphi) = V_{AB^+} + V_{is} + V_{an} \quad (3)$$

where  $R$  is the center of mass distance,  $r$  the internal diatom coordinate, and  $\varphi$  the angle between the  $R$  and  $r$  axes. The first term in Eq. (3) is a Morse function for the isolated  $AB^+$  diatom, with parameters determined from spectroscopic data [14]. The second term represents a long-range ion-induced dipole attraction and a short-range exponential repulsion between  $M$  and  $AB^+$

$$V_{\text{is}}(R) = E \exp(-\beta R) - \frac{C_4}{2R^4} [1 - \tanh(R - R_o)] \quad (4)$$

The third, anisotropic term describes the chemical interaction between the atom  $M$  and atoms  $A$  and  $B$ , respectively. As described (though in verbal form) in [13] we represent it as

$$V_{\text{an}}(R, r, \varphi) = \sum_{i=1}^2 D_i \exp[-\alpha_i(R_i - R_i^*)] \{ \exp \times [-\alpha_i(R_i - R_i^*)] - 2 \exp[-\Delta_i(\gamma_i - \gamma_i^*)^2] \} \quad (5)$$

where  $R_{1,2}$  are the distances between the atom  $M$  and the atoms  $A$  and  $B$ , respectively, and  $\gamma_i$  are the angles between  $R_i$  and the  $r$  axes. (The relations between  $R$ ,  $r$ ,  $\varphi$ , and  $R_i$ , and  $\gamma_i$  are given in [15]). The factors  $\Delta_i$ , for convenience, are presented in the form

$$\Delta_i = -\ln(0.1)/\theta_i^2 \quad (6)$$

where the “anisotropy widths”  $\theta_i$ , in the absence of any additional information can be regarded as adjustable parameters, like in [13]. To obtain the values of the potential parameters, we proceeded in analogy to [7] and [8].

The only difference consists in some enlargement (about 20%) of the values of the total bond energy  $D_o$  and in the incremental bond energies  $D_i$ , leaving the electrostatic interaction unchanged. We believe, this should partially take into account the complexity of the  $CH_4$ , which results in an enlargement of the collision time and in enlarged vibrational relaxation rate constants at low  $KE_{\text{cm}}$  values.

The values of all interaction potential parameters are given in Table 1. All dynamical calculations were performed using the FORTRAN program ADIAV [16] which realizes to the full extent the formalism of the

Table 1

Potential parameters of the  $NO^+(v)-CH_4$  interaction potential

$E$	8802 eV	$R_1^*$	3.695 Å
$\beta$	3.292 Å <sup>-1</sup>	$R_2^*$	3.713 Å
$C_4$	18.43 eV Å <sup>4</sup>	$\gamma_1^*$	104°
$R_o$	15.0 Å	$\gamma_2^*$	105°
$D_i$	0.2905 eV	$\theta_i$	20°
1. $\alpha_i$	1.647 Å <sup>-1</sup>		

classical path model. The essence and the detailed algorithm of the model are presented in Billing's publications (see, for review, [9]).

Thus only a very brief summary of the method will be given here. The relative translational and rotational motion of the diatom are treated classically, whereas the vibration is quantized. The total wave function for the quantum-mechanical part of the problem is expanded in Morse eigenstates of the diatom. In turn, the equations of motion for the classical part of the problem are coupled through the effective intermolecular potential to the differential equations for the amplitudes of the vibrational transitions.

As appropriate for the whole energy range studied, the following values of the input parameters were adopted: the initial center-of-mass distance was set to  $R_{\text{init}} = 20$  Å, the maximum impact parameter was estimated to be  $b_{\text{max}} = 5$  Å, the number of Morse oscillator states included in the expansion of the total wave function was set to  $N = 7$ . In the final dynamic calculations the batches of about 500 trajectories for each energy value were calculated, which yields statistical error bars smaller than 20% for the cross sections, and even less for the rate constants.

#### 4. Results and discussion

The experimental results obtained for the quenching rate constants  $k_{10}$  and  $k_{43}$  for processes (1) and (2) are shown in Fig. 2 together with earlier results [6]. Both rate constants show a pronounced minimum at several tenths of an electron volt, and  $k_{43}$ , is larger than  $k_{10}$  at all energies investigated.

The accuracy of the present data is assumed to be  $\pm 30\%$ . The main uncertainties arise from the mobility data of  $NO^+(v)$  in He [we assume that the mobility

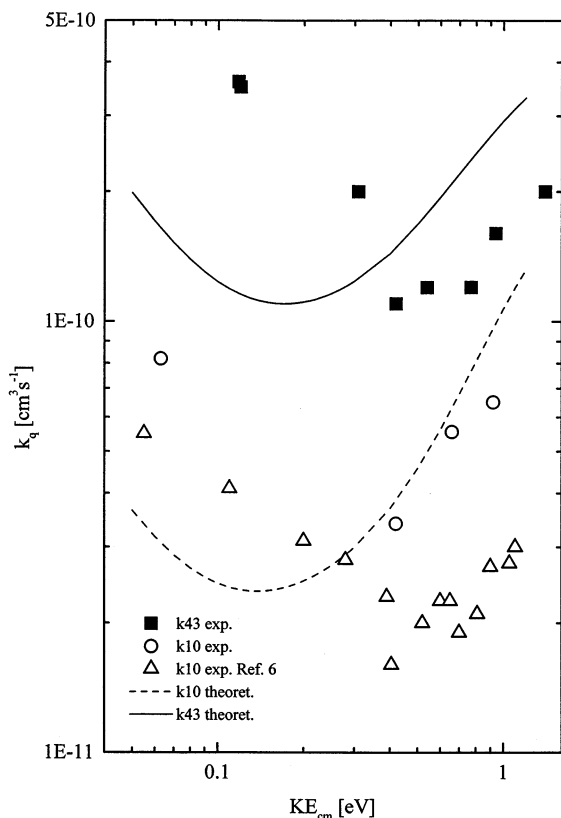


Fig. 2. Comparison of experimental (present work and Ref. [6]) and theoretical (present work) rate constants  $k_q$  for vibrational relaxation of  $\text{NO}^+$  ( $v$ ) in collisions with  $\text{CH}_4$ .

of  $\text{NO}^+$  ( $v = 0$ ) is the same as the one of  $\text{NO}^+$  ( $v = 1, 2, 3, \dots$ ) which is not necessarily the case] and from the inaccuracy in the flow rates of  $\text{CH}_4$  added to the buffer gas. Furthermore, in the case of process (1) also contributions from quenching of  $\text{NO}^+$  ( $v = 2, 3, 4, \dots$ ) to  $\text{NO}^+$  ( $v = 0$ ) in sequential or direct processes may contribute to the apparent rate constant. These contributions however are limited due to the strongly declining population of  $\text{NO}^+$  ( $v$ ) with increasing  $v$ . The total concentration of  $\text{NO}^+$  ( $v = 0$ ) was about 50% of all  $\text{NO}^+$  and the concentration of  $\text{NO}^+$  ( $v \geq 4$ ) was less than 10% of all  $\text{NO}^+$  thus we assume that the density of  $\text{NO}^+$  ( $v \geq 2$ ) only makes up for about 25% of all  $\text{NO}^+$ . Part of that,  $\text{NO}^+$  ( $v = 2$ ), is quenched to  $\text{NO}^+$  ( $v = 1$ ) which then needs a second quenching step to contribute to  $k_{10}$ . Even if the quenching rate constant  $k_{21}$  is higher than  $k_{10}$  by

a factor of 2 the overall contribution of higher vibrational states  $\text{NO}^+$  ( $v = 2, 3, 4, \dots$ ) to  $k_{10}$  should be less than 15%. Thus the assumed overall accuracy of the present experimental data being  $\pm 30\%$  seems to be justified.

For comparison of the theoretical results with the experimental data for both investigated vibrational transitions, also the calculated values  $k_{43}$  and  $k_{10}$  are shown in Fig. 2. The theoretical data reproduce the overall shape of the corresponding experimental ones, showing pronounced minima in the kinetic energy,  $\text{KE}_{\text{cm}}$ , dependence of the rate constants, though at lower energies than in the experimental case. Also quantitatively the experimental and theoretical rate constants agree within a factor of about 2 in the middle and high energy ranges. A somewhat larger deviation between experimental and theoretical data in the low energy range finds its partial explanation in our simplification of the actual collision dynamics. Taking fully into account the complexity of  $\text{NO}^+-\text{CH}_4$  interaction would facilitate the complex formation, and hence the vibrational relaxation of  $\text{NO}^+$  ( $v$ ) at low energies.

Summarizing, the experimentally found kinetic energy dependence of the rate constants for vibrational relaxation of  $\text{NO}^+$  ( $v$ ) in collisions with  $\text{CH}_4$ , showing a pronounced minimum at some tenths of an electron volt, is confirmed by the present calculations in the framework of realistic, though approximate, theoretical models for both interaction potential and collision dynamics. Taking into account the complexity of the studied collision system, the achieved semiquantitative agreement between theory and experiment can be regarded as satisfactory in the whole energy range investigated.

## Acknowledgements

This work was supported by the Austrian Fonds zur Förderung der Wissenschaftlichen Forschung under project no. P12429 and by the Danish Natural Sciences Research Council. One of the authors (V.A.Z.) expresses his gratitude to the Institut für Ionenphysik for financial support and warm hospitality during his stay in Innsbruck.

## References

- [1] E.E. Ferguson, *J. Phys. Chem.* 90 (1986) 731.
- [2] W. Lindinger, *Int. J. Mass Spectrom. Ion Processes* 80 (1987) 115.
- [3] W. Dobler, W. Federer, F. Howorka, W. Lindinger, M. Durup-Ferguson, E.E. Ferguson, *J. Chem. Phys.* 79 (1983) 1543.
- [4] R.A. Morris, A.A. Viggiano, F. Dale and J.F. Paulson, *J. Chem. Phys.* 88 (1988) 4772.
- [5] W. Federer, W. Dobler, F. Howorka, W. Lindinger, M. Durup-Ferguson, E.E. Ferguson, *J. Chem. Phys.* 83 (1985) 1032.
- [6] R. Richter, W. Lindinger, E.E. Ferguson, *J. Chem. Phys.* 89 (1988) 5692.
- [7] V.A. Zenevich, S.K. Pogrebnya, W. Lindinger, M. Cacciatore, *Int. J. Mass Spectrom. Ion Processes* 129 (1993) 101.
- [8] V.A. Zenevich, W. Lindinger, S.K. Pogrebnya, M. Cacciatore, G.D. Billing, *J. Chem. Phys.* 102 (1995) 6669.
- [9] G.D. Billing, *Comput. Phys. Rep.* 1 (1984) 237.
- [10] E.A. Gislason and E.E. Ferguson, *J. Chem. Phys.* 87 (1987) 6474.
- [11] H. Böringer, M. Durup-Ferguson, D.W. Fahey, F.C. Fehsenfeld, E.E. Ferguson, *J. Chem. Phys.* 79 (1983) 4201.
- [12] M. McFarland, D.L. Albritton, F.C. Fehsenfeld, E.E. Ferguson, A.L. Schmeltekopf, *J. Chem. Phys.* 59 (1973) 6610, 6620, 6629.
- [13] P. Tosi, M. Ronchetti, A. Lagana, *Chem. Phys. Lett.* 136 (1987) 398.
- [14] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
- [15] V.A. Zenevich, W. Lindinger, G.D. Billing, *Chem. Phys. Lett.* 197 (1992) 99.
- [16] G.D. Billing, *Comp. Phys. Comm.* 32 (1984) 45.