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International Journal of Mass Spectrometry 184 (1999) 75–81



# Isotope effects in the ion/molecule capture

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Received 20 August 1998; accepted 4 October 1998

## Abstract

Calculations indicate that ion–molecule reactions in gases exhibit marked kinetic isotope effects. Whereas at high temperatures the effects are normal (the lighter molecule reacts faster than the heavier one), at low temperatures the reversed isotope effect is predicted: a heavier isotopomeric molecule reacts with an ion faster than the lighter one. (Int J Mass Spectrom 184 (1999) 75–81) © 1999 Elsevier Science B.V.

*Keywords:* Ion/molecule reaction; Kinetic isotope effect

## 1. Introduction

Capture of an ion by a linear molecule is governed by the long-range part of the interaction potential,  $V$ , that, in turn, depends on the distance  $r$  between the mass centres of an ion and a molecule and on the angle  $\gamma$  between the  $r$  axis and the direction of the dipole moment,  $\mu$  (or quadrupole moment,  $Q$ ) of the molecule. The  $V$  potential also depends on the coefficients that characterize the ion/molecule pair, such as the electric charge on the ion,  $q$ ; the isotropic polarisability of the molecule,  $\alpha$ ; the dipole or quadrupole moment of the molecule; the moment of inertia of the molecule,  $I$ ; and so on. Only if the molecule is spherically symmetric is the dependence of  $V$  on  $r$  simple, and expressed by the well known, so called Langevin capture rate constant,  $k_L$  [1]

$$k_1 \equiv k_L = 2\pi q(\alpha/M)^{1/2} \quad (1)$$

where  $M$  stands for the reduced mass of the ion/molecule pair.

In the classical approach that ignores quantization of the orbital momentum the reduced capture rate constant for the nonspherical molecule, defined  $\kappa_1 \equiv k_1/k_L$ , becomes a function of two dimensionless parameters. In the quantum approach this number increases to three parameters. In choosing the dimensionless parameters, one of the two alternative versions can be followed. The first one stems from the work of Chesnavich, Bowers, and Su [2]; for a dipolar molecule  $x_1 \equiv (\mu^2/2\alpha kT)^{1/2}$  and  $\xi \equiv M\alpha q/I\mu$  whereas for a quadrupolar molecule  $b_3 \equiv (Q^4 q^4/2kT\alpha^3 q^6)^{2/3}$  and  $\zeta \equiv M\alpha^2 q^2/IQ^2$ . Such a parametrization was used widely in the calculations using trajectory integration (TC), transition state theory (TST), and statistical adiabatic channel model (SACM) [3–10]. Recently, another parametrization

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was suggested by Troe, Nikitin, and their co-workers [11–13]. The reduced capture rate constant,  $\kappa_1$ , is expressed as the function of two parameters,  $M$  and  $\Theta$ , where  $M \equiv \xi x_1^2$  and  $\Theta \equiv 0.25/x_1^2$  for the dipolar molecules, and  $M \equiv \zeta(b_3)^{8/3}$  and  $\Theta \equiv (b_3)^{-4/3}$  for the quadrupolar molecules. Both sets of parametrization are correct and the choice between them is a matter of taste or convenience.

If quantization of the orbital momentum is taken into account, the reduced capture rate constant also becomes dependent on the third parameter that is defined  $y \equiv (2I\mu^2/\alpha\hbar^2)^{1/2}$  for the dipolar molecules and  $y \equiv (IQ^4/\alpha^3q^2\hbar^2)^{1/2}$  for the quadrupolar molecules [14,15]. Because the effects associated with quantization of the orbital momentum are important only at low temperatures,  $y$  determines the low temperature behaviour of  $\kappa_1$ . According to Troe [14,15] for the dipolar molecules

$$\lim_{T \rightarrow 0} \kappa_1 = (1 + y^2/3)^{1/2} \quad (2)$$

Practically, Eq. (2) describes the behaviour of the capture rate constant at characteristic rotational temperature,  $\sim 0.1$ – $15$  K. At higher temperatures, say at room temperature,  $\kappa_1 = f(x_1, \xi)$  or  $\kappa_1 = g(b_3, \zeta)$ . For physically realistic ion/molecule reactions  $\xi$  or  $\zeta$  attain fairly large values,  $0.1$ – $1000$ . Calculations indicate that the changes in either  $\xi$  or  $\zeta$  affect  $\kappa_1$  only if the former values are small, say  $10^{-4}$ – $10^{-1}$ . Thus, over the range of not very low temperatures  $\kappa_1$  depends only on  $x_1$  (dipolar molecules) or on  $b_3$  (quadrupolar molecules). If so, the classical reduced capture rate constant should not depend on the isotopic composition of the molecule, since isotopic substitution results only in the change of the reduced mass and the moment of inertia, and none of these values is present in the definition for  $x_1$  and  $b_3$ . To support this conclusion, many examples can be found in the reported experimental and calculated ion/molecule reaction rates. For instance, analytical representation of trajectory calculations concerned with the reaction of acetylenes with  $H_3^+$  clearly shows that the classical dependence  $\kappa_1(T)$  is the same for all of the isotopomeric acetylenes [12]. The same conclusion

can be extended to the dipolar isotopomeric molecules such as, for instance, HCl, DCl, and TCl.

Whereas the ratio  $k_1/k_L$  does not depend on the isotopic composition,  $k_L$  does, inasmuch as the reduced mass of the reacting system is effected, because the proportionality to  $1/\sqrt{M}$  is obeyed. It follows from the definition of the reduced mass that the effect can only be important if the mass of the molecule is small compared with the mass of the ion. Experimental data for the rate constants of such ions as  $D_2^+$ ,  $He^+$ ,  $O^+$ ,  $N_2^+$ ,  $CD_3^+$ ,  $ArD^+$ ,  $Ar^+$ ,  $Ar_2^+$ ,  $Cl^+$ , and  $F^+$  with  $H_2$ , HD, and  $D_2$  are in good agreement with such expectations. On the other hand, if the ion/molecule reaction involves a small ion and a large molecule any difference in the reduced mass of the system becomes vanishingly small. For instance,  $M(H_3^+ - HCl) = 4.60 \times 10^{-24}$  g and  $M(H_3^+ - DCl) = 4.61 \times 10^{-24}$  g; the effect of isotopic composition of the molecule is negligible. All in all, the classical theories of the rate of ion/molecule reactions predict some importance of isotope effects. Because  $k_1$  depends on the reduced mass of the reacting pair, the smaller the mass of the reacting molecule, the larger the effect. The effects are predicted to be normal; substitution with a heavier isotope leads to deceleration of the capture rate.

Note that at very low temperatures the classical approach ceases to be adequate. According to Eq. (2) not only  $M$  but also the moment of inertia starts to affect the capture rate constant through the  $y$  parameter. The moment of inertia is very sensitive to the changes in isotopic substitution. The range of very low temperatures attracts considerable attention from the point of view of cosmochemistry, geochemistry, atmospheric chemistry, and geochronology. In this article we attempt to throw more light on the isotope effects in ion/molecule reactions at very low temperatures.

## 2. Calculations and discussion

The simplest method to account for the quantization of orbital momentum is the statistical adiabatic channel model (SACM). According to this model the

microcanonical capture rate constant,  $\kappa_1(E)$ , can be expressed as [16]

$$\kappa_1(E) \equiv \frac{k_1(E)}{k_L} = \frac{1}{y\xi} \cdot \frac{1}{\sqrt{2Z_E} \cdot \rho_r(Z_E)} \sum_k g_k h(E - E_{0k}) \quad (3)$$

where

$$\rho_r(Z_E) = \sum_j (2j+1)h \cdot \left(1 - \frac{j(j+1)}{Z_E}\right) \sqrt{1 - \frac{j(j+1)}{Z_E}} \quad (4)$$

Here,  $g_k$  is the degeneration of the state labeled with  $k$ ;  $h(x)$  is the Heaviside function;  $\eta = y\xi$  for the capture of the dipolar molecule, and  $\eta = \sqrt{2y} \zeta$  for the capture of the quadrupolar molecule;  $Z_E = 2IkT/\hbar^2$  whereas  $E_{0k}$  is the threshold energy of the  $k$ th state

$$E_{0k} = \max_{R=R_0} [V_k(R)] \quad (5)$$

$V_k(R)$  is the potential of the  $k_{th}$  reaction channel that can be obtained by solving the Schrödinger equation

$$\hat{H}\psi_{k\lambda} = V_k(R) \cdot \psi_{k\lambda} \quad (6)$$

The Hamiltonian  $\hat{H}$  for the ion/molecule system can be expressed as [16]

$$\frac{\hat{H}}{E} = \sqrt{\frac{2}{Z_E}} \cdot \frac{1}{\eta} \left\{ \frac{\hat{\ell}_z^2}{R^2} + \frac{\eta}{\sqrt{2Z_E}} \cdot \hat{h} \right\} \quad (7)$$

$$\hat{h} = \hat{j} + \hat{v}(R, \gamma) - \frac{Z_E}{R^4} \quad (8)$$

$\hat{v}(R, \gamma)$

$$= \left\{ \begin{array}{l} -\sqrt{2Z_E} \cdot y \cdot \frac{\cos \gamma}{R^2} \quad \text{for a dipole} \\ (yZ_E^3)^{1/4} \cdot \frac{(3 \cos^2 \gamma - 1)}{R^3} \quad \text{for a quadrupole} \end{array} \right\} \quad (9)$$

where  $\hat{\ell}$  and  $\hat{j}$  are the operators for the orbital and rotational momenta, respectively.

Table 1

A set of the molecular parameters for the compounds of interest in this work

$\mathcal{M}$	$\alpha(\mathcal{M})$	$\mu(\mathcal{M})$	$Q(\mathcal{M})$	$I(\mathcal{M})$
HCl	2.56	1.086	—	2.64
DCl	2.56	1.086	—	5.14
TCl	2.56	1.086	—	7.51
HBr	3.49	0.827	—	3.28
DBr	3.49	0.827	—	6.48
TBr	3.49	0.827	—	9.60
HI	5.20	0.447	—	4.26
DI	5.20	0.447	—	8.46
TI	5.20	0.447	—	12.59
HCN	2.58	2.98	—	18.91
DCN	2.58	2.98	—	23.11
TCN	2.58	2.98	—	27.05
C <sub>2</sub> H <sub>2</sub>	3.33	—	7.20	23.82
C <sub>2</sub> HD	3.33	—	7.20	28.39
C <sub>2</sub> D <sub>2</sub>	3.33	—	7.20	33.31
C <sub>2</sub> HT	3.33	—	7.20	32.62
C <sub>2</sub> T <sub>2</sub>	3.33	—	7.20	42.79
C <sub>2</sub> DT	3.33	—	7.20	37.88

For physically realistic ion/molecule systems, the  $\eta$  coefficient is large because both  $y$  and  $\xi$  (or  $\zeta$ ) are large. Therefore, at not too large energies, the second term in Eq. (7) will far exceed the first term. Under such conditions the Born–Oppenheimer approxima-

Table 2

Dimensionless parameters that characterize the capture of H<sub>3</sub><sup>+</sup> by the polar molecules

Reactions	$\xi$	$y$
HCl + H <sub>3</sub> <sup>+</sup> →	19.34	15.09
DCl + H <sub>3</sub> <sup>+</sup> →	9.95	21.06
TCl + H <sub>3</sub> <sup>+</sup> →	6.83	25.46
HBr + H <sub>3</sub> <sup>+</sup> →	29.69	10.75
DBr + H <sub>3</sub> <sup>+</sup> →	15.04	15.11
TBr + H <sub>3</sub> <sup>+</sup> →	10.15	18.40
HI + H <sub>3</sub> <sup>+</sup> →	63.66	5.44
DI + H <sub>3</sub> <sup>+</sup> →	32.09	7.66
TI + H <sub>3</sub> <sup>+</sup> →	21.56	9.34
HCN + H <sub>3</sub> <sup>+</sup> →	0.99	108.20
DCN + H <sub>3</sub> <sup>+</sup> →	0.81	119.62
TCN + H <sub>3</sub> <sup>+</sup> →	0.69	129.41
HCl + e <sup>-</sup> →	3.8 × 10 <sup>-3</sup>	15.09
DCl + e <sup>-</sup> →	1.9 × 10 <sup>-3</sup>	21.06
TCl + e <sup>-</sup> →	1.3 × 10 <sup>-3</sup>	25.46
HBr + e <sup>-</sup> →	5.6 × 10 <sup>-3</sup>	10.75
DBr + e <sup>-</sup> →	2.8 × 10 <sup>-3</sup>	15.11
TBr + e <sup>-</sup> →	1.9 × 10 <sup>-3</sup>	18.40

Table 3  
Dimensionless parameters that characterize the capture of  $H_3^+$  by the quadrupolar acetylene isotopomers

Reaction	$\zeta$	$y$
$C_2H_2 + H_3^+ \rightarrow$	0.925	82.22
$C_2HD + H_3^+ \rightarrow$	0.779	89.75
$C_2D_2 + H_3^+ \rightarrow$	0.666	97.21
$C_2HT + H_3^+ \rightarrow$	0.680	96.22
$C_2T_2 + H_3^+ \rightarrow$	0.522	110.18
$C_2DT + H_3^+ \rightarrow$	0.588	103.68

tions can be used to solve the Schrödinger equation. The  $k$  number that labels the eigenvalues in such approximations is the set of three quantum numbers:  $k = \{l, j, m\}$  where  $|m| \leq j$ . For some particular systems that feature very small  $\eta$ , the Born–Oppenheimer approximation cannot be used. The rigorous solution obtained by the variational Ritz method [16] depends on  $k = \{l, j, J\}$  where  $J = |\mathbf{l} + \mathbf{j}|$ .

The microcanonical capture rate constant  $\kappa_1(E)$  estimated this way can be averaged thermodynamically using the appropriate statistical weight [16] that yields the temperature dependent capture rate constant,  $\kappa_1(T)$ . To inspect the temperature dependence, the reactions of  $H_3^+$  ions with either isotopomeric hydrogen halides: (HCl, DCl, TCl), (HBr, DBr, TBr), (HI, DI, TI), and (HCN, DCN, TCN) or with acety-

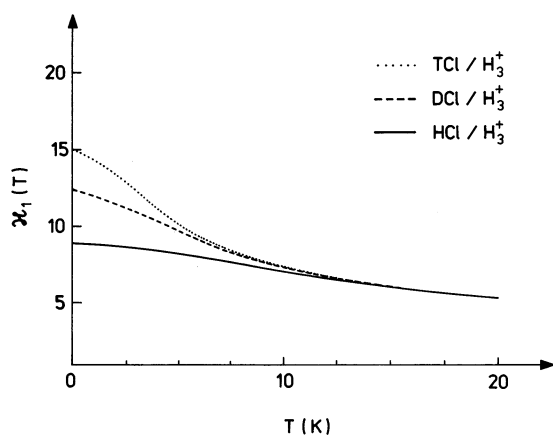


Fig. 1. Temperature dependence of the reduced capture rate constant estimated by SACM for the reaction of  $H_3^+$  with isotopomeric HCl. Calculations employed the Born–Oppenheimer approximations. Parameters that characterize the reactions are listed in Table 2.

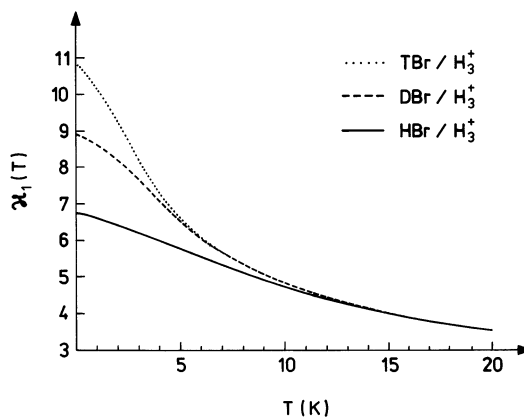


Fig. 2. Temperature dependence of the reduced capture rate constant estimated by SACM for the reaction of  $H_3^+$  with isotopomeric HBr. Calculations employed the Born–Oppenheimer approximations. Parameters that characterize the reactions are listed in Table 2.

lene with different combinations of hydrogen atoms were selected. The molecular parameters for such molecules are assembled in Table 1.

Combined with the reduced mass of the ion/molecule pair, such molecular parameters define the dimensionless parameters, either  $\xi$  and  $y$  or  $\zeta$  and  $y$ . These are listed in Tables 2 and 3. It is clearly seen that typical ion/molecule reactions are characterized by fairly large values for  $\xi$  and  $y$  ( $\zeta$  and  $y$ ). Only when

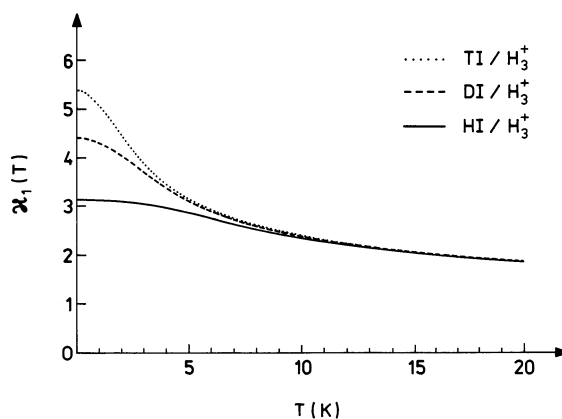


Fig. 3. Temperature dependence of the reduced capture rate constant estimated by SACM for the reaction of  $H_3^+$  with isotopomeric HI. Calculations employed the Born–Oppenheimer approximations. Parameters that characterize the reactions are listed in Table 2.

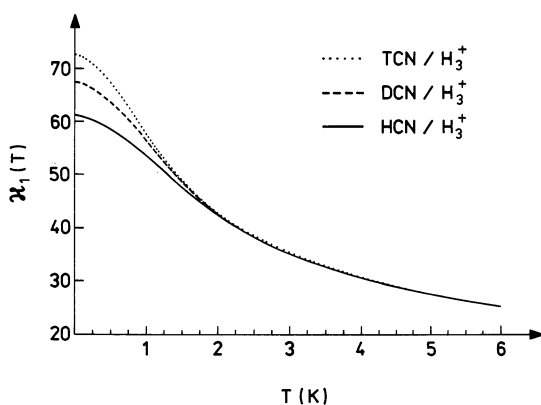


Fig. 4. Temperature dependence of the reduced capture rate constant estimated by SACM for the reaction of  $\text{H}_3^+$  with isotopomeric HCN. Calculations employed the Born–Oppenheimer approximations. Parameters that characterize the reactions are listed in Table 2.

the electron is involved does the  $\xi$  or  $\zeta$  parameter become very small, and then the Born–Oppenheimer approximations have to be discarded.

The choice of the reactions to be investigated is not

accidental. The following criteria were taken into account. First, a wide spectrum of molecular properties is represented: the molecules are either polar or nonpolar; the systems feature large and small values for  $\xi$ . Second, the mass of the reacting molecule is always much larger than the mass of the captured ion; hence, kinetic effects associated with the change in the reduced mass can be ignored. Third, these reactions have been studied extensively both theoretically and experimentally [10,15,17].

Figs. 1–4 show the temperature dependence of the reduced capture rate constant for the capture of the  $\text{H}_3^+$  ion by the isotopomers of the polar molecules (hydrogen halides as well as hydrogen cyanide). Fig. 5 describes the analogous dependence for the isotopomers of the acetylene molecule. Successive figures describe the estimates of  $\kappa_1(T)$  obtained in this work for the model systems characterized by extremely small values for  $\xi$ . Such systems can be identified as  $e^- + \text{hydrogen chlorides}$  and  $e^- + \text{hydrogen bromides}$ . Two series of calculations were performed; the results of accurate calculations are given in Fig. 6

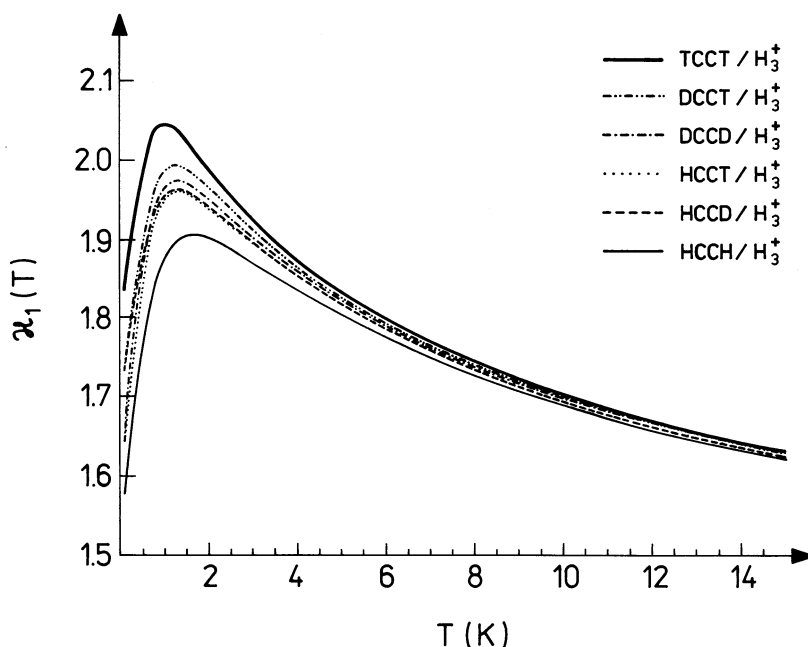


Fig. 5. Temperature dependence of the reduced capture rate constant estimated by SACM for the reaction of  $\text{H}_3^+$  with isotopomeric acetylenes. Calculations employed the Born–Oppenheimer approximations. Parameters that characterize the reactions are listed in Table 2.

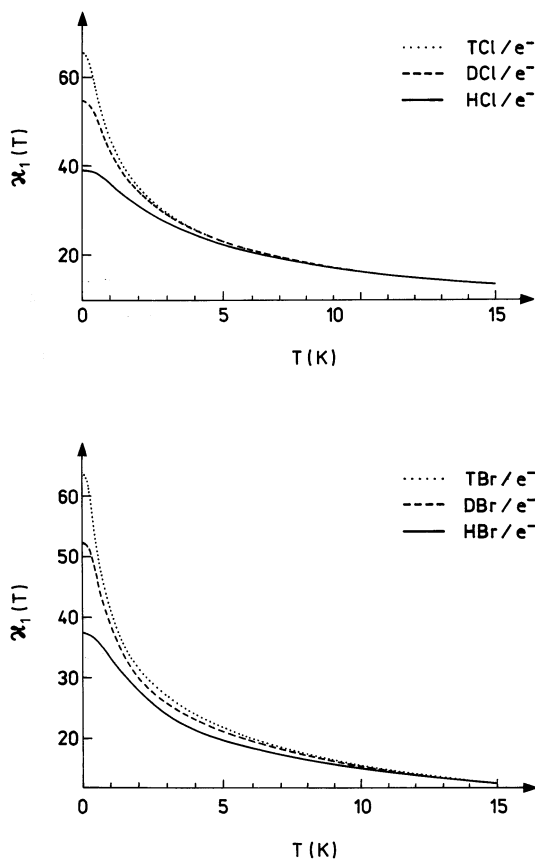


Fig. 6. Temperature dependence of the reduced capture rate constant estimated by SACM for the reaction of  $e^-$  with (a) isotopomeric HCl, and (b) isotopomeric HBr. Calculations were accurate without using the Born–Oppenheimer approximation.

whereas those using the Born–Oppenheimer approximations are given for comparison in Fig. 7.

All the results indicate that at high temperatures the isotopic composition does not affect  $\kappa_1(T)$ . Such a degeneration persists down to the temperature in the vicinity of the characteristic rotational temperature of the lightest isotopomer,  $\Theta_r \equiv \hbar^2/2Ik$ . Close to this temperature the curves for the heavier isotopomers split from that for the lightest one. Second split occurs at even lower temperature, in the vicinity of the  $\Theta_r$  characteristic for the medium isotopomer. For instance, in the reactions of hydrogen chlorides, the  $\kappa_1$  ( $H_3^+ + HCl$ ) curve splits from the other two curves at a temperature of 15 K [ $\Theta_r$  (HCl) = 15.2 K] whereas

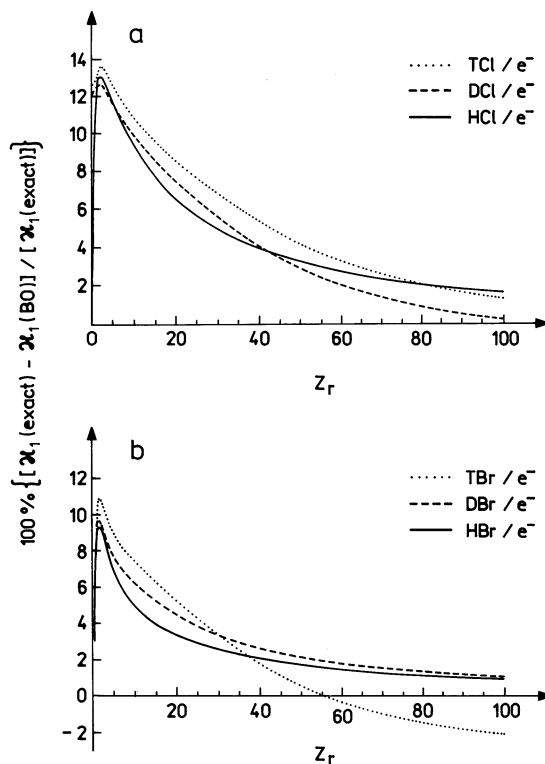


Fig. 7. Dependence of the relative difference between the reduced capture rate constant estimated accurately and that obtained with use of the Born–Oppenheimer approximation on the reduced temperature,  $Z_r \equiv 2IRT/\hbar^2$ , for the reactions of  $e^-$  with (a) isotopomeric HCl, and (b) isotopomeric HBr.

$\kappa_1(H_3^+ + DCl)$  splits from  $\kappa_1(H_3^+ + TCl)$  at a temperature of 8 K [ $\Theta_r$  (DCl) = 7.8 K]. The remaining hydrogen halides as well as hydrogen cyanide exhibit similar behaviour. In all of the cases examined the curve for the lighter isotopomer occupies a position lower than those for the heavier isotopomers. In other words, at low temperatures the heavier the molecule the faster the reaction. Such an isotope effect can be termed the reversed isotope effect, because typically (though by no means universally) substitution with the heavier isotope results in deceleration of the reaction rate ( $H_2 + Cl_2$  occurs faster than  $D_2 + Cl_2$ ). The occurrence of the reversed isotope effect has already been suggested in [18]. Also, the low temperature bound to  $\kappa_1$  estimated for the ion/dipole captures by Troe [14,15] indicates the occurrence of such an effect.

Note that as the temperature decreases, the curves shown in Figs. 1–4 tend to the limiting value given by Eq. (2) (developed by Troe [9,10]), but the behaviour of  $\kappa_1$  at  $T \rightarrow 0$  shown in Fig. 5 is different.  $\kappa_1(T)$  for acetylenes increases as the temperature decreases reaching a maximum in the vicinity of the characteristic rotational temperature  $\Theta_r$ . As the temperature decreases further, so does the  $\kappa_1$ . This type of dependence is typical for the reaction of an ion with a quadrupolar molecule [8]. According to Troe [8], the low temperature bound to  $\kappa_1$  in the captures of quadrupoles is 1, i.e.  $\kappa_1(T \rightarrow 0) = 1$ . The value for this bound notwithstanding, it is shown in Fig. 5 that a nonpolar molecule such as acetylene exhibits, like the polar molecules, the reversed kinetic isotope effect. Apparently, such an effect is a feature of all kinds of ion/molecule reactions at very low temperatures. This conclusion can be extended to include the hypothetical ion/molecule reactions characterized by very small values for  $\xi$ . As already mentioned, the capture of a thermal electron by a molecule seems to belong to this class of reactions. At very small  $\xi$ , the nonadiabatic effects associated with coupling of the orbital and rotational momenta can be of some importance [11,16]. For this reason the Born–Oppenheimer approximation that ignores this coupling is not adequate, and more accurate calculations are necessary. A typical behaviour of  $\kappa_1(T)$  for the capture of  $e^-$  by the isotope substituted hydrogen chlorides and bromides is shown in Fig. 6(a) and (b). Such unusual captures are also characterized by the reversed kinetic isotope effect at low temperatures; the heavier molecule captures the electron faster than the lighter one. Compared with the typical systems that feature large values for  $\xi$  there is another striking difference: the capture occurs much faster and the low temperature upper bound to the capture rate constant is much larger than that estimated according to Troe [8]. To estimate the contribution of nonadiabatic effects, the calculations employing the Born–Oppenheimer approximation were also performed. The relative error in estimation of  $\kappa_1$  using the Born–Oppenheimer approximation is shown in Fig. 7(a) and (b) in

dependence on the reduced temperature,  $Z_r = 2IkT/\hbar^2$ . The contribution of nonadiabatic motion is seen not to exceed  $\sim 10\%$  at low temperatures, and dwindles down to  $\sim 1\text{--}2\%$  at room temperature.

### 3. Conclusions

(1) At very low temperatures all kinds of ion/molecule reactions exhibit the reversed kinetic isotope effect; the heavier molecule captures an ion faster than the lighter one. (2) Such an effect becomes important starting from the temperature that corresponds to the characteristic rotational temperature of the lightest isotopomer. (3) The unusual ion/molecule captures that feature very small values for  $\xi$  occur much faster than the typical processes characterized by the large values for  $\xi$ .

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