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Calculation of interchange reaction rates by a 'nearest resonance' method

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Abstract. Thermal and suprathermal energy gas reaction rates for exothermic processes involving molecules or molecular ions are treated generally in terms of the adiabatic criterion. An absolute cross section function is derived in terms of a near-resonance energy defect which allows the determination of the dependence of reaction rate on temperature under conditions of complete or partial thermodynamic equilibrium. The reaction rates for seventeen exothermic processes are evaluated at 300 °K and in many cases over a temperature range 150 °K–4800 °K: (i) under complete temperature equilibrium, (ii) with vibrational and rotational temperatures 300 °K and (iii) at various vibrational temperatures of the diatomic partner but at a fixed translational and rotational temperature of $T = 300$ °K. Special attention is given to aeronomically important reactions.

It is apparent from these calculations that the exit channels of the triatomic quasi-molecule of collision are sufficiently well determined by the energy levels of the infinitely separated initial reactants to make the consideration of such levels useful in predicting reaction cross sections.

1. Introduction

It is well known that thermal energy gas reaction rates for exothermic processes of the type

$$X + YZ \rightarrow XY + Z \tag{1}$$

where both X and YZ may be neutral, but one may be ionized, may differ from each other by orders of magnitude for not easily discernable reasons. In this paper we discuss these processes, ion–atom interchange as well as charge transfer and atom–atom interchange, in terms of the Massey near-adiabatic criterion (Massey 1949). The magnitude of the cross section for a reaction is then determined essentially from a comparison of the time $\tau_t = h/|\Delta E|$ of the electronic transition involving an energy change equal to the energy defect ΔE of the reaction and the time $\tau_c = a/v$ of collisions. Here a is a collision length known as the adiabatic parameter and v is the velocity of impact. Only for $\tau_t \ll \tau_c$ is adiabatic adjustment of the collidant wave functions possible and the probability of transition between initial and final states small. But although a qualitative behaviour of a particular cross section may be obtained from this criterion, it gives no information on absolute cross sections.

The adiabatic criterion was found to hold in the form of a maximum rule (Hasted 1951) for atomic charge-transfer processes, with $a = 7$ Å. The maximum cross section occurs when $\tau_t = \tau_c$. This rule is consistent (Lee and Hasted 1965) with semi-classical impact parameter calculations (Rapp and Francis 1962) which, although relatively crude in that semi-empirical atomic orbitals are used, give surprisingly good agreement with experiment, even in the near-thermal energy region.

Although the near-adiabatic resonance criterion has proved to be a qualitatively useful guide for atomic collisions, there has been some doubt as to its applicability to gaseous reactions of the type of equation (1). Many such reactions involving electronic transitions, as well as many ion–molecule dissociative charge-transfer reactions, have been found to occur rapidly at thermal energies. These results are contrary to what is expected on the basis of Massey's adiabatic hypothesis, on the assumption that the collision products are formed without internal excitation.

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It is the proposal of the authors that, owing to added rotational and vibrational degrees of freedom, low energy collisions involving molecules, in which the rotational and vibrational levels are merely broadened and not made to overlap, are dominated by 'accidental resonance' conditions in which $\tau_t \simeq \tau_c$. Since many thermal energy collisions take place with inward spiralling orbits except at the largest impact parameters, τ_c is larger than is the case in non-spiralling collisions; therefore for accidental resonance ΔE must be very small, probably only a few wave numbers. The electronic transition in this case involves an energy change equal to the energy defect corresponding to the closest exothermic resonance with a given vibrational–rotational energy level of the reactant molecule, and not equal to the ground-state energy defect of the reaction. As a result, the adiabatic region is often subthermal. In exothermic processes it is often possible to find an accidental near-resonance when the products are formed in vibrationally and rotationally excited states, but it is more likely when the nearest product rotational quantum number J is smallest, since the separation of levels increases with J.

Impact parameter calculations of charge transfer (Rapp and Francis 1962) show that as the impact velocity decreases from the value for which $\tau_t = \tau_c$ the cross section falls monotonically. A simple approximate expression for the cross section σ has been found to fit experimental atomic charge-transfer data (Hasted 1959) in this impact velocity region:

$$\sigma = A \exp\left(-\frac{k'a|\Delta E|}{hv}\right) \tag{2}$$

with A, k' constants. Since this expression is only justifiable empirically and in any case does not hold in the far adiabatic region, it has not been widely used, except for two-electron capture processes (Kozlov and Bondor 1966). It is nevertheless particularly suitable for rough approximation to processes dominated by accidental resonance.

The maximum value of the cross section, σ_m, may for ion–molecule reactions be calculated directly from the inward-spiralling orbit equation (Gioumousis and Stevenson 1958)

$$\sigma_m = \frac{\pi}{v}\left(\frac{4\alpha e^2}{\mu}\right)^{1/2} \tag{3}$$

for collisional reduced mass μ, electronic charge e and target polarizability α (Rothe and Bernstein 1959, Parkinson 1960). This is substituted in equation (2):

$$\sigma_m(v_m) = A \exp\left(-\frac{k'a|\Delta E|}{hv_m}\right). \tag{4}$$

For neutral reactions σ_m is calculated using the impact parameter method developed for charge transfer (Rapp and Francis 1962), as discussed in § 2.5 below.

The velocity v_m at which the maximum cross section is reached may be calculated from the equality $h/|\Delta E| = a/v_m$, with adiabatic parameter a determined empirically, but $a \gg 7$ Å on account of the spiralling orbits. For $v \geqslant v_m$, $\sigma = \sigma_m$ is taken as a sufficiently good approximation. For $v \leqslant v_m$, A is eliminated from equations (2) and (4) to give

$$\sigma = \sigma_m(v_m) \exp k'\left(1 - \frac{a|\Delta E|}{hv}\right). \tag{5}$$

In the present treatment of molecular processes ΔE is taken to be the smallest energy defect, corresponding to the closest exothermic resonance with a given vibrational–rotational energy sublevel of the reactant molecule. Equation (5), therefore, approximates the absolute cross section for the transition between specific energy sublevels of the reactant and product molecules.

2. Calculation of the near-resonance cross section

The data available in the literature on atomic and molecular constants used in these calculations are given in tables 1(*a*) and 1(*b*). Ionization potentials, dissociation energies and vibrational and rotational constants have been taken from Herzberg (1950) unless otherwise indicated.

All calculations were carried out on the University College IBM 360/65 computer.

Table 1(*a*). Molecular constants

Molecule	I (ev)	Dissociation energy (ev)	Rotational and vibrational constants B_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	α_e
$N_2(x\ ^1\Sigma_g^+)$	15·576	9·756	1·9987	2358·07	14·188	−0·0124†	0·0187
$O_2(x\ ^3\Sigma_g^-)$	12·063	5·080	1·4457	1580·36	12·073	+0·0546	0·0158
$NO(x\ ^2\Pi_{3/2})$	9·266¶	6·487	1·7046	1904·03	13·97	−0·0012	0·0178
$NO(x\ ^2\Pi_{1/2})$				1903·68			
$CO(x\ ^1\Sigma^+)$	14·013‡	11·108	1·9314	2170·21	13·461	+0·0308	0·0175
$N_2^+(x\ ^2\Sigma_g^+)$			1·9322	2207·19	16·136	−0·0400	0·0202
$O_2^+(x\ ^2\Pi_g)$			1·6722	1876·4	16·53	0·0	0·0198
$NO^+(x\ ^1\Sigma^+)$			2·002	$2378{\cdot}70_3$	16·647§	0·0	—
$CO^+(x\ ^2\Sigma^+)$			1·9772	2214·24	15·164	−0·0007	0·0190

† Lofthus 1960.

‡ Callomon 1967, private communication.

§ Miescher 1967, private communication; W. R. Simmons, *University of Colorado* AFCRL 65–670.

¶ Dressler and Miescher 1966.

Table 1(*b*). Atomic energy levels

Atomic state	Ionization potential I (ev)	Atomic state	Term level (cm^{-1})
$N(^4S^o_{3/2})$	14·545	$O(^3P_2)$	0·0
$O(^3P_2)$	13·615	$O(^3P_1)$	158·5
$Ar(^2P_{3/2})$	15·756	$O(^3P_0)$	226·5
Atomic state	Term level (cm^{-1})		
$N(^4S^o_{3/2})$	0·0	$O(^1D)$	15867·7
$N(^2D_{5/2})$	19223	$O(^1S)$	33792·4
$N(^2D_{3/2})$	19231	$O^+(^4S^o_{3/2})$	0·0
$N(^2P^o_{3/2,1/2})$	28840	$Ar(^1S_0)$	0·0
$N^+(^3P_0)$	0·0	$Ar^+(^2P_{3/2})$	0·0
$N^+(^3P_1)$	49·1	$Ar^+(^2P_{1/2})$	1432
$N^+(^3P_2)$	131·3		

2.1. *Energy levels*

The vibrational quantum states of the reactant and product molecule or ion are calculated from the term values of the anharmonic oscillator, which are given by

$$G(v) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3. \tag{6}$$

Here v is the vibrational quantum number and ω_e, $\omega_e x_e$ and $\omega_e y_e$ are the vibrational constants of the electronic level.

The rotational quantum states of the vibrational level are calculated from the term values of the rigid rotator, which are given by

$$F_v(J) = B_e J(J+1) \tag{7}$$

and the vibrating rotator, which are given by

$$F_v(J) = B_v J(J+1). \tag{8}$$

Here J is the rotational quantum number and B_v is the rotational constant in the vibrational level v, given by

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) \tag{9}$$

where B_e is the rotational constant corresponding to the equilibrium separation r_e and α_e is a third rotational constant.

2.2. *Population distribution*

For a neutral or ionic molecular gas in thermal equilibrium the number of molecules N_v in the vibrational level v is given by

$$N_v = \frac{N}{Q_v}\exp\left\{-\frac{G(v)hc}{kT}\right\}. \tag{10}$$

Here h, c, k and T are respectively Planck's constant, the velocity of light, the Boltzmann constant and the absolute temperature. N is the total number of molecules in all vibrational levels, and Q_v is a normalization factor corresponding to the state sum (or partition function) which is given by

$$Q_v = \sum_{v=0}^{\infty}\exp\left\{-\frac{G(v)hc}{kT}\right\}. \tag{11}$$

The number of molecules N_{vJ} in the rotational level J of the vibrational level v at the temperature T is given by

$$N_{vJ} = \frac{N}{Q_v Q_r}(2J+1)\exp\left[-\frac{\{G(v)+F_v(J)\}hc}{kT}\right] \tag{12}$$

where each state has a $(2J+1)$-fold degeneracy and Q_r is the rotational state sum. This simplifies to

$$N_{vJ} = \frac{N_v}{Q_r}(2J+1)\exp\left\{-\frac{F_v(J)hc}{kT}\right\} \tag{13}$$

which implies that the distribution over the rotational levels in each vibrational level is the same, but the absolute population of all the rotational levels in the particular vibrational level is considerably smaller than for the lowest vibrational level, corresponding to the factor $\exp\{-G(v)hc/kT\}$.

2.3. *Determination of the contributing near-resonances*

For the general case of an exothermic process of the type

$$\mathrm{X}+\mathrm{YZ}(v, J) \rightarrow \mathrm{XY}(v', J')+\mathrm{Z} \tag{14}$$

the energy defect is given by the equation

$$\begin{aligned}\frac{\Delta E}{hc}(v, J \rightarrow v', J') = \frac{\Delta E}{hc}(0, 0 \rightarrow 0, 0) - \{G'(v')-G'(0)\} \\ +\{G(v)-G(0)\}-\{F'(J')-F(J)\}\end{aligned} \tag{15}$$

where $\Delta E(0, 0 \rightarrow 0, 0)$ represents the energy defect at infinite separation for the case when both the reactant and product molecules are in the ground state vibrationally and rotationally.

Since $\Delta E(0, 0 \rightarrow 0, 0)$ is actually a function of the separation of the colliding particles, the correct value of ΔE should correspond to the separation at which the transition occurs or is most probable. However, for reasons discussed at the end of this paper the value of $\Delta E(0, 0 \rightarrow 0, 0)$ at infinite separation has been employed in the initial calculations.

In the actual calculation for an exothermic process with a given energy defect $\Delta E(0, 0 \rightarrow 0, 0)$ a computer programme is set up to choose the appropriate vibrational–rotational levels in the product molecule which will give the six smallest energy defects $\Delta E(v, J \rightarrow v', J')$ corresponding to the six closest exothermic resonances with a given vibrational–rotational energy level of the reactant molecule. These six energy defects $n = 1$–6 all contribute to the cross section at a given impact velocity, but nearly always the nearest one or two resonances dominate. Calculations taking into account only the nearest four resonances give almost identical results.

This procedure is repeated for each vibrational–rotational energy level of the reactant molecule weighted with the distribution function

$$f(v, J) = \frac{1}{Q_{\mathrm{v}} Q_{\mathrm{r}}}(2J+1) \exp\left[-\frac{\{G(V)+F_v(J)\}hc}{kT}\right] \tag{16}$$

calculated between the limits $J = 0$ and $J = 30$, $v = 0$ and $v = 20$.

2.4. *The cross section for equilibrium and non-equilibrium conditions*

The contribution to the total cross section of a vibrational–rotational level of the reactant molecule is given by

$$\begin{aligned} \sigma_{v,J}(v) &= \sigma_{\mathrm{m}}(v_{\mathrm{m}}) f(v, J) \exp\left[k'\left\{1 - \frac{a|\Delta E|(v, J \rightarrow v', J')}{hv}\right\}\right], \qquad v \leqslant v_{\mathrm{m}} \\ &= \sigma_{\mathrm{m}}(v_{\mathrm{m}}) f(v, J) \qquad v \geqslant v_{\mathrm{m}}. \end{aligned} \tag{17}$$

The total cross section for the reaction is then

$$\sigma(v) = \sum_{v,J} \left\{\sum_{n=1}^{n=6} \sigma_{v,J} f(v, J)\right\} \Big/ \sum_{v,J} f(v, J). \tag{18}$$

The variation of the total cross section for reaction with temperature under conditions of translational, rotational and vibrational temperature equilibrium can now be calculated, since the velocity distribution function is dependent only on temperature.

Furthermore, the vibrational and rotational parts of the exponential in the expression for the distribution function can be separated, thus allowing the treatment of non-equilibrium conditions. In special cases the reactants are not in complete thermodynamic equilibrium; the kinetic, rotational and vibrational gas temperatures (respectively T, T_{r}, T_{v}) may all be different. The distribution function (equation (16)) will then take the form

$$f(v, J) = \frac{1}{Q_{\mathrm{v}} Q_{\mathrm{r}}}(2J+1) \exp\left\{-\frac{G(v)hc}{kT_{\mathrm{v}}}\right\} \exp\left\{-\frac{F_v(J)hc}{kT_{\mathrm{r}}}\right\} \tag{19}$$

2.5. *Calculation of* σ_{m}

The proposals of Rapp and Francis (1962) for symmetrical resonance charge transfer at thermal energies have been shown (Hasted 1968) to be successful in approximate terms. The approach adopted in the present calculations is that the chemical transition is between two different states of the collision pseudo-molecule; usually it involves the transition of one electron, as is the case in the charge-transfer collision; therefore the same proposals should be applicable.

Rapp and Francis (1962) chose at each impact velocity the largest of two cross sections, the spiralling-orbit cross section σ_0 (equation (3)) and the rectilinear-orbit cross section σ_{RF} of equation (20) below. At the temperatures with which we are concerned here, σ_0 is usually the larger, but not by very much. For ion–molecule reactions, we choose $\sigma_{\mathrm{m}} = \sigma_0$, taking no account of the rectilinear-orbit cross section. It is found that this gives best agreement with the experimental temperature functions. For neutral reactions, it is probable that orbiting does not contribute nearly so strongly, and we therefore choose $\sigma_m = \sigma_{RF}$:

$$\sigma_{RF}^{1/2} = 10^{-8} \exp\{1{\cdot}208(3{\cdot}466 - \lg \mathscr{I})\} - 5{\cdot}627 \times 10^{-8} \mathscr{I}^{-1/2} \lg v \tag{20}$$

where $\mathscr{I}$ is the average ionization potential (ev) of the collision pair and v is the relative velocity given by equation (25) with mean velocity

$$\bar{v} = 1{\cdot}45 \times 10^4 \left(\frac{T}{\mu}\right)^{1/2} \text{cm s}^{-1} \tag{21}$$

where μ is the reduced mass (a.m.u.) and T the kinetic temperature. By analogy with the average ionization potential $\frac{1}{2}\{I(\mathrm{X}) + I(\mathrm{YZ})\}$, for charge-transfer collisions, we write for ion–atom interchange

$$\mathscr{I} = \tfrac{1}{2}\left\{I(\mathrm{X}) + \frac{I(\mathrm{Y}) + I(\mathrm{Z})}{2}\right\} \tag{22}$$

and for atom–atom interchange

$$\mathscr{I} = \tfrac{1}{3}\{I(\mathrm{X}) + I(\mathrm{Y}) + I(\mathrm{Z}) + 2E_a(\mathrm{X}) + E_a(\mathrm{Y}) + E_a(\mathrm{Z}) + E_a(\mathrm{YZ})\} \tag{23}$$

where E_a are electron affinities in electron volts (negative numbers). Equation (22) is actually superfluous to the present calculations, since we take $\sigma_m = \sigma_0$ for ion–atom interchange.

3. Results

The computer calculations have been carried out for a number of different values of the adiabatic parameter a and the constant k'. The most suitable values for the parameters a and k' have been determined empirically. It is found (Bohme *et al.* 1967 a) that for ion–atom interchange and charge transfer $a = 100$ Å and $k' = 2$ and for atom–atom interchange $a = 200$ Å and $k' = 2$ are the most suitable values.

The constant k' is a measure of the 'sharpness' of the maximum in the individual cross section function. For high-energy atomic-charge-transfer data $k' \simeq 1$ is appropriate (Hasted 1959), but $k' = \frac{1}{4}$ is sometimes incorrectly assumed. The present calculations fit the data best with $k' = 2$. Low-energy charge-transfer maxima are often 'sharper' (Edmonds and Hasted 1964) than those at high energies, but no detailed theoretical reason has been advanced; possibly curve-crossing is involved.

3.1. *Room-temperature reaction rate constants*

In thermal equilibrium the rate constant k is related to the collision cross section

$$k = \frac{\int f(v)\sigma(v)v \, dv}{\int f(v) \, dv} \tag{24}$$

$$f(v) = \frac{4}{\pi^{1/2}} \frac{v^2}{\bar{\bar{v}}^3} \exp\left(-\frac{v^2}{\bar{\bar{v}}^2}\right) \tag{25}$$

where the most probable velocity

$$\bar{\bar{v}} = \left(\frac{2kT}{\mu}\right)^{1/2}.$$

Thermal energy rate constants have been computed using the rigid rotator model for the processes tabulated in table 2, and the results are compared graphically in figure 1 with experimental data (Bohme *et al.* 1967 b, Clyne and Thrush 1961, Fehsenfeld *et al.* 1965, 1966 a, b, Ferguson *et al.* 1965 a, b, Goldan *et al.* 1966, Phillips and Schiff 1962, Sparks 1966, unpublished, Warneck 1967). For certain processes which terminate in more than

Table 2

(1) $\mathrm{Ar}^+({}^2\mathrm{P}^\circ_{3/2,1/2}) + \mathrm{CO}(\mathrm{x}\ {}^1\Sigma^+) \rightarrow \mathrm{CO}^+(\mathrm{x}\ {}^2\Sigma^+) + \mathrm{Ar}({}^1\mathrm{S}_0)$

(2) $\mathrm{Ar}^+({}^2\mathrm{P}^\circ_{3/2,1/2}) + \mathrm{NO}(\mathrm{x}\ {}^2\Pi_\mathrm{r}) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+,\ \mathrm{a}\ {}^3\Sigma^+) + \mathrm{Ar}({}^1\mathrm{S}_0)$

(3) $\mathrm{Ar}^+({}^2\mathrm{P}^\circ_{3/2,1/2}) + \mathrm{N}_2(\mathrm{x}\ {}^1\Sigma_\mathrm{g}^+) \rightarrow \mathrm{N}_2{}^+(\mathrm{x}\ {}^2\Sigma_\mathrm{g}^+) + \mathrm{Ar}({}^1\mathrm{S}_0)$

(4) $\mathrm{Ar}^+({}^2\mathrm{P}^\circ_{3/2,1/2}) + \mathrm{O}_2(\mathrm{x}\ {}^3\Sigma_\mathrm{g}^-) \rightarrow \mathrm{O}_2{}^+(\mathrm{x}\ {}^2\Pi_\mathrm{g}) + \mathrm{Ar}({}^1\mathrm{S}_0)$

(5) $\mathrm{N}^+({}^3\mathrm{P}_{0,1,2}) + \mathrm{CO}(\mathrm{x}\ {}^1\Sigma^+) \rightarrow \mathrm{CO}^+(\mathrm{x}\ {}^2\Sigma^+) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2})$

(6) $\mathrm{N}^+({}^3\mathrm{P}_{0,1,2}) + \mathrm{O}_2(\mathrm{x}\ {}^3\Sigma_\mathrm{g}^-) \rightarrow \mathrm{O}_2{}^+(\mathrm{x}\ {}^2\Pi_\mathrm{g}) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2},\ {}^2\mathrm{D}^\circ_{5/2,3/2})$

(7) $\mathrm{N}^+({}^3\mathrm{P}_{0,1,2}) + \mathrm{NO}(\mathrm{x}\ {}^2\Pi_\mathrm{r}) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+,\ \mathrm{a}\ {}^3\Sigma^+) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2},\ {}^2\mathrm{D}_{5/2,3/2},\ {}^2\mathrm{P}^\circ_{3/2,1/2})$

(8) $\mathrm{O}^+({}^4\mathrm{S}^\circ_{3/2}) + \mathrm{O}_2(\mathrm{x}\ {}^3\Sigma_\mathrm{g}^-) \rightarrow \mathrm{O}_2{}^+(\mathrm{x}\ {}^2\Pi_\mathrm{g}) + \mathrm{O}({}^3\mathrm{P}_{2,1,0})$

(9) $\mathrm{O}^+({}^4\mathrm{S}^\circ_{3/2}) + \mathrm{NO}(\mathrm{x}\ {}^2\Pi_\mathrm{r}) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+) + \mathrm{O}({}^3\mathrm{P}_{2,1,0},\ {}^1\mathrm{D}_2,\ {}^1\mathrm{S}_0)$

(10) $\mathrm{N}^+({}^3\mathrm{P}_{0,1,2}) + \mathrm{O}_2(\mathrm{x}\ {}^3\Sigma_\mathrm{g}^-) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+,\ \mathrm{a}\ {}^3\Sigma^+) + \mathrm{O}({}^3\mathrm{P}_{2,1,0},\ {}^1\mathrm{D}_2,\ {}^1\mathrm{S}_0)$

(11) $\mathrm{O}^+({}^4\mathrm{S}^\circ_{3/2}) + \mathrm{N}_2(\mathrm{x}\ {}^1\Sigma_\mathrm{g}^+) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2})$

(12) $\mathrm{N}_2{}^+(\mathrm{x}\ {}^2\Sigma_\mathrm{g}^+) + \mathrm{O}({}^3\mathrm{P}_{2,1,0}) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2},\ {}^2\mathrm{D}^\circ_{5/2,3/2})$

(13) $\mathrm{O}_2{}^+(\mathrm{x}\ {}^2\Pi_\mathrm{g}) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2}) \rightarrow \mathrm{NO}^+(\mathrm{x}\ {}^1\Sigma^+) + \mathrm{O}({}^3\mathrm{P}_{2,1,0},\ {}^1\mathrm{D}_2,\ {}^1\mathrm{S}^0)$

(14) $\mathrm{N}_2{}^+(\mathrm{x}\ {}^2\Sigma_\mathrm{g}^+) + \mathrm{O}({}^3\mathrm{P}_{2,1,0}) \rightarrow \mathrm{O}^+({}^4\mathrm{S}^\circ_{3/2}) + \mathrm{N}_2(\mathrm{x}\ {}^1\Sigma_\mathrm{g}^+)$

(15) $\mathrm{N}_2{}^+(\mathrm{x}\ {}^2\Sigma_\mathrm{g}^+) + \mathrm{N}({}^4\mathrm{S}^\circ_{3/2}) \rightarrow \mathrm{N}_2(\mathrm{x}\ {}^1\Sigma_\mathrm{g}^+) + \mathrm{N}^+({}^3\mathrm{P}_{0,1,2})$

(16) $\mathrm{N}({}^4\mathrm{S}^\circ_{3/2}) + \mathrm{NO}(\mathrm{x}\ {}^2\Pi_\mathrm{r}) \rightarrow \mathrm{N}_2(\mathrm{x}\ {}^1\Sigma_\mathrm{g}^+) + \mathrm{O}({}^3\mathrm{P}_{2,1,0},\ {}^1\mathrm{D}_2)$

(17) $\mathrm{N}({}^4\mathrm{S}^\circ_{3/2}) + \mathrm{O}_2(\mathrm{x}\ {}^3\Sigma_\mathrm{g}^-) \rightarrow \mathrm{NO}({}^2\Pi_\mathrm{r}) + \mathrm{O}({}^3\mathrm{P}_{2,1,0})$

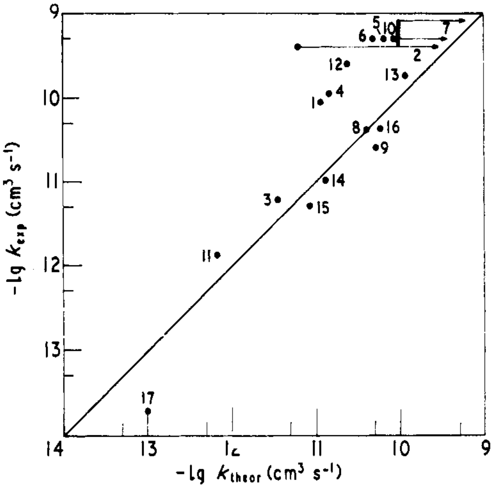

Figure 1. Comparison of experimental and calculated rate constants for processes (1)–(17) (key in table 2). Where experimental limits are published, the points are represented as vertical lines. Horizontal arrows attached to points 2, 7 and 10 indicate that an enhancement of the calculated rate is to be expected, because no account has been taken of excited product NO⁺ a $^3\Sigma^+$, whose spectroscopic data are not known with sufficient precision for calculations to be made. For process (17), $T_{\mathrm{exp}} = 500$ °K, $T_{\mathrm{calc}} = 300$ °K.

one electronic level the computed rate is a summation of the rates for each, except where the statistical weight factor is zero, as is the case for certain excited products of processes (9), (13) and (16). The collidant fine-structure sub-levels are equally weighted (Ar^+ $J = \frac{3}{2}, \frac{1}{2}$), but this is open to criticism, since the participation of the higher energy sub-levels is sometimes precluded, for incompletely understood reasons (Scott and Hasted 1964, Hussain and Kerwin 1965). All product fine-structure sub-levels are included as separate channels.

In atomic charge transfer it is usual (Rapp and Francis 1962) to multiply the calculated cross section by a statistical weight factor, equal to the ratio of number of configurations of the quasi-molecule of collision able to pass directly to the product states to the total number of configurations which can be formed from the collidant states (Herzberg 1966). We find that such a procedure does not weaken the importance of the adiabatic criterion in interpreting the experimental data, but it does lower nearly all the calculated rate constants until they are smaller than the experimental data. In these calculations no statistical weight factor has been included, in the belief that this is indirect evidence that transitions between different configurations of the quasi-molecule can occur in trinuclear systems.

It is arguable that processes (8), (10), (11), (13), (15) and (17) are able to proceed in two ways, namely with interchange of either of the two atoms of the homologous molecular species; however, the calculated rates have not been multiplied by a factor of 2 to conform with this argument.

3.2. *The reaction rate constant as a function of vibrational temperature*

As has been indicated in § 2.4, it is possible to calculate the dependence of thermal energy reaction rates on vibrational excitation only. In this case the translational and rotational temperatures of the reactant molecules are held constant at $T = 300$ °K.

Recent laboratory experiments have shown that the $T = 300$ °K rate constant for the ion–atom interchange reaction (11),

$$O^+(^4S^o_{3/2}) + N_2(X\,^1\Sigma_g^+) \rightarrow NO^+(X\,^1\Sigma^+) + N(^4S^o_{3/2}) \qquad (27)$$

is greatly increased when the N_2 is vibrationally excited (Schmeltekopf *et al.* 1967). Figure 2 compares the calculated reaction rate constant as a function of the N_2 vibrational temperature with the experimental data. There is reasonable agreement. It is significant that the experimental evidence indicates that the vibrational distribution of N_2 created by the microwave discharge is reasonably close to a Boltzmann distribution so that an effective temperature can be implied. It is difficult to assess the importance of rotational excitation in these experiments, although the relatively high rotational relaxation rate ensures rapid equilibration to room temperature.

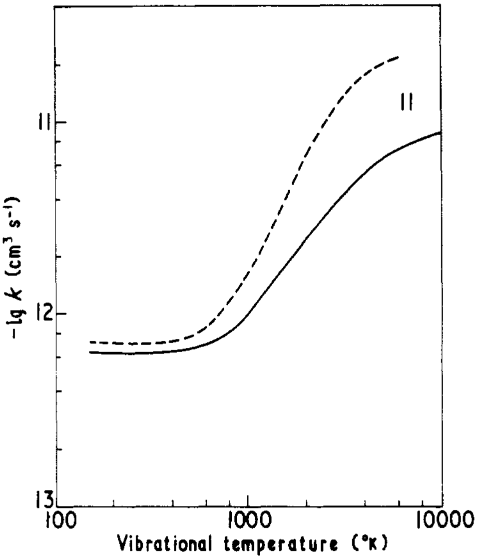

Figure 2. Comparison of experimental and calculated rate constants for process (11), with varying vibrational temperature. Broken curve, experimental data (Schmeltekopf *et al.* 1967); full curve, calculated values.

Although the rigid rotator calculations give fair agreement with the experimental results (figures 1, 2, 7 and 8), this is not so true in the case of vibrating rotator calculations. The rotational quantum levels of the vibrational level v, when calculated from the term values of the vibrating rotator, are closer together than those calculated from the term values of the rigid rotator. The overall effect is, for example, that the total summed rate constant for reaction (11) will be larger at all temperatures considered (figure 8). The rate constant for this reaction is dependent on the value of α_e (equation (9)) especially at lower vibrational temperatures. An accurate spectroscopic value of α_e for NO^+ was not available in the literature. Hence computer calculations have been made for reaction (11) in which α_e was varied over a large range (0·0–0·0500) with special emphasis being given to the region of values in the vicinity of the expected value of $\alpha_e(\sim 0{\cdot}0200)$. The corresponding values for the rate constant at 300 °K varied over two orders of magnitude non-monotonically. It is a striking feature of these calculations that the rigid rotator model seems to be the most appropriate in this and other cases.

A classical consideration of the collision complex in which the primary ion is spiralling around the neutral particle in nearly circular orbits under the influence of an inverse fourth-power polarization field yields a value for the period of one complete revolution $\tau_0 \sim 10^{-14}$ s. The period for one vibration of a typical molecule is $\tau_v \geqslant 10^{-14}$ s. The spiralling ion therefore makes one or more complete revolutions during the period of one vibration and 'sees' effectively a rigid rotator during that time. The orbiting ion may damp the vibration of the molecule through the coupling of its angular momentum with the internal energy of the molecule.

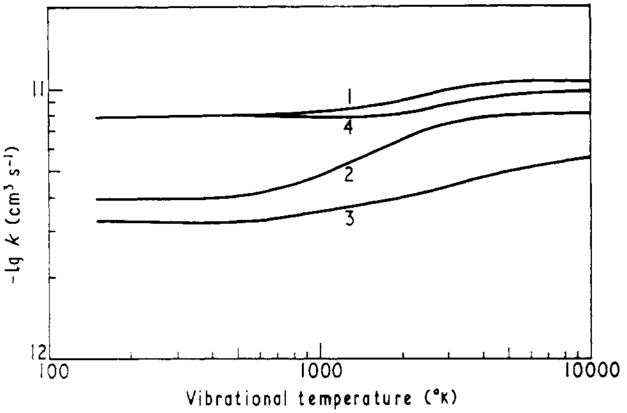

Figure 3. Calculated rate constants for processes (1)–(4), with varying vibrational temperature.

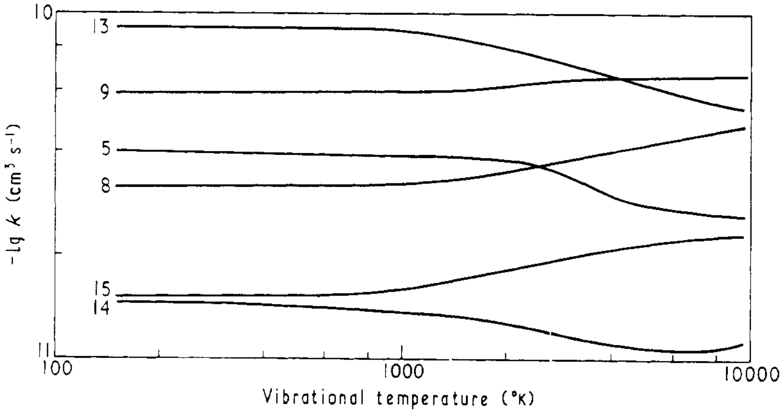

Figure 4. Calculated rate constants for processes (5), (8), (9) and (13)–(15) with varying vibrational temperature.

The dependence of the rate constant on the vibrational temperature of the primary molecule or ion is shown in figures 3 and 4 for other processes. The rotational and translational temperatures are constant at $T = 300$ °K. A comparison of these rigid rotator calculations with experiment is, as yet, not possible.

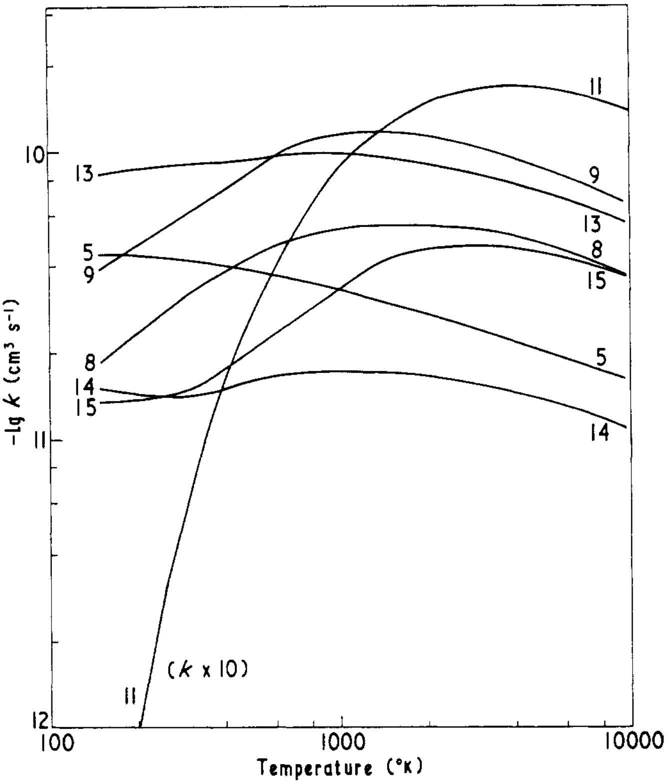

Figure 5. Calculated rate constants for processes (5), (8), (9), (11) and (13)–(15) with full temperature variation.

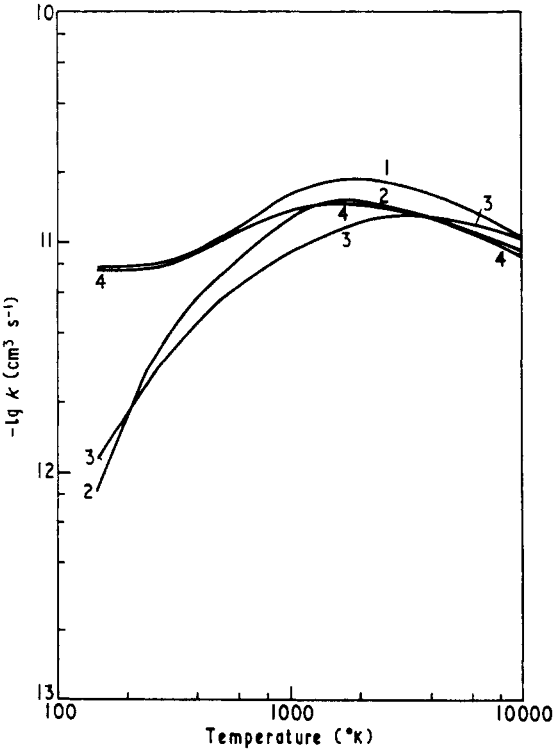

Figure 6. Calculated rate constants for processes (1)–(4) with full temperature variation.

3.3. *Rate constants for varying kinetic temperature and for full temperature variation*

Calculations have been made with full temperature variation (kinetic collisional, vibrational and rotational). The results are shown in figures 5 and 6. There is at present very little experimental data with which they can be compared, but flowing afterglow data will shortly become available, involving temperature variation of the entire experiment.

Calculations have also been made with variation only of the kinetic temperature (rotational and vibrational temperature held at 300 °K). These are comparable not only with mass spectrometer source measurements, but with drift tube data (Bohme *et al.* 1967 b,

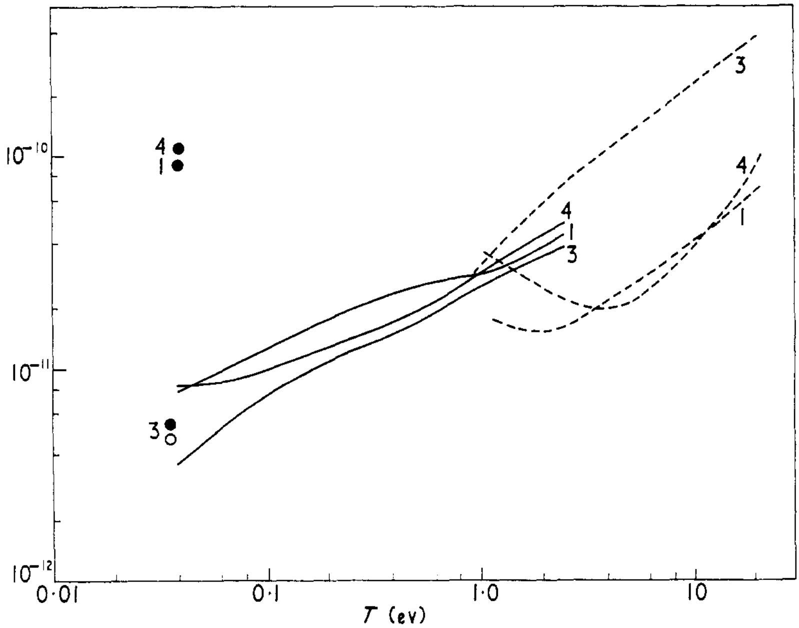

Figure 7. Comparison of experimental and calculated rate constants for processes (1), (3) and (4) with kinetic temperature variation. Broken curves, unpublished experimental data of the authors. Full curves, calculated values. Full circles, experimental afterglow data (Fehsenfeld *et al.* 1966 a). Open circle, Knewstubb (1968, private communication).

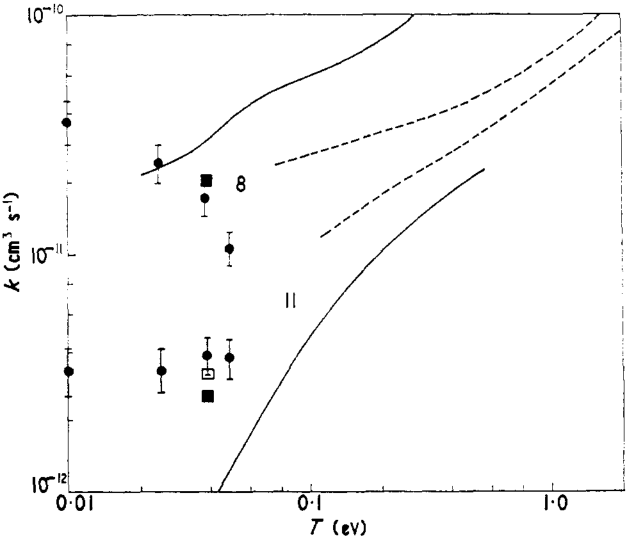

Figure 8. Comparison of experimental and calculated rate constants for processes (8) and (11), with kinetic temperature variation. Full lines, calculated values. Broken curves and full circles, Nakshbandi and Hasted (1967). Open square, Fehsenfeld *et al.* 1965; full square, Copsey *et al.* 1966.

Ong and Hasted 1968) in which the kinetic temperature is varied electrically whilst the gas temperature is held constant. Results are shown in figures 7 and 8.

4. Discussion

The empirical choice of k' and a, as well as the decision to put $\sigma_m = \sigma_0$ and not choose for σ_m the largest of the two values σ_0 and σ_{RF}, and the decision not to include statistical weight factors (Rapp and Francis 1962), have all been dictated by lengthy comparisons of calculations with experimental data. In the preliminary calculations (Bohme *et al.* 1967 a) only 300 °K data were taken into account, but in the present work it has been found that data with kinetic temperature variation are a much more sensitive test. Our original values of k' and a still stand, but it has been found that choosing $\sigma_m = \sigma_0$ is necessary if the rate of increase of k with temperature is to be kept down to within reach of the experimental values. In particular the experimental falling of k in processes (1), (4) and (8) is not reproduced in these calculations, and, since it is faster than the orbiting equation (3), it could only be explained by some feature not envisaged in the present calculations, possibly pseudo-crossing of potential energy surfaces.

It might be argued that endothermic resonances in which the energy difference is made up from the kinetic energy of impact will contribute to the summations. We have made full calculations involving this assumption and report that the correspondence with experiment is adversely affected. In particular processes (11) (both T and T_v dependence), (17) (full temperature dependence), as well as the calculated cross sections in figure 1, are raised by amounts which cause us to reject the endothermic resonance contribution hypothesis. Conversion of collisional orbiting momentum to internal energy would appear to be difficult, as is the case at energies just above threshold in phase-space calculations (Wolf 1966) of ion–atom interchange.

Nevertheless, there is reason to be encouraged by the present, rather crude, methods of calculation. It will be possible to combine them with similar non-spiralling-orbit collision calculations, computing classically the dependence of collision time upon impact parameters, and inferring a suitable distribution of adiabatic parameters.

A significant prediction of the present approach is that the product molecule will be dominantly in the vibrational–rotational state determined by the energy difference ΔE of the exothermic collision. Many exothermic atom–atom interchange reactions of type (1) have been shown by experiment to yield vibrational excitation in the product molecule. The vibrationally excited molecules have been studied by absorption or emission spectroscopy, chemical reactivity, and crossed molecular beams. The production of vibrationally excited molecules in the ground electronic states by collisional processes has been discussed in detail by Dalgarno with specific reference to aeronomy (Dalgarno 1963). There is sufficient evidence to indicate that atom–atom interchange reactions usually result in the formation of strongly vibrating molecules. However, few spectrosco picstudies were performed in which the mean collision time was much longer than the radiative lifetime of the product molecule. As a result, collisional deactivation was sufficient to perturb an absolute measurement of vibrational excitation in the products. Considerably more accurate information on the excitation energy of the products can be obtained from the measurement of the angular distribution of the products. Datz and Schmidt (1967) have made a crossed molecular beam study of the reaction

$$D + Br_2 \rightarrow DBr^v + Br. \tag{28}$$

From their experimental results they inferred that the bulk of the DBr observed is excited to the maximum attainable vibrational–rotational state (in this case the ninth vibrational level). Similar results were obtained for alkali–halogen systems (Minturn *et al.* 1966).

In crossed-beam ion–molecule reaction experiments it has not yet been possible to infer the excitation of the products quantitatively, although one experiment (Doverspike *et al.* 1966) has come close to it, and the stimulus to solve this problem experimentally is great.

A consideration of a simple valence-bond resonance description of the activated complex in atom–atom interchange reactions, coupled with experimental and theoretical evidence concerning the efficiency of transfer of vibrational energy at a collision, has led Polanyi

(1959) to predict that almost the entire exothermicity of reaction will be contained in vibration of the bond being formed, and to discuss ten particular cases of exothermic atom–atom interchange reactions, in each of which some experimental evidence exists for the presence of more than equilibrium vibration in the bond formed.

On the other hand Smith (1959), on the basis of a purely classical treatment, predicts that the maximum fraction of the exothermicity of an atom–atom interchange reaction available for high vibrational modes is limited by a kinematic factor $\sin^2\beta$ where β is the angle of rotation required to take a coordinate system suitable for describing the reactants into one suitable for describing the products. The kinematic factor depends only on the masses m_X, m_Y and m_Z of the atoms involved and can be calculated from the relation

$$\tan^2\beta = \frac{m_Y}{m_X}+\frac{m_Y}{m_Z}+\frac{m_Y^2}{m_X m_Z}. \tag{29}$$

This model is successful in predicting the highest vibrational level produced in most of the reactions considered by Smith. From the expression for $\tan^2\beta$, it is evident that transfer into high vibrational states will be most efficient when the atom being exchanged is much heavier than at least one of its partners; and, conversely, that transfer will be least efficient when the central atom is much lighter than both its neighbours.

A criticism that is frequently made of the usefulness of the adiabatic criterion is that in the usual formulation, adopted in § 1 of this paper, the energy defects ΔE_{eff} which are effective during the collision process are assumed equal to those maintaining at infinite nuclear separation, ΔE_∞. This is obviously not correct, and may lead to particularly serious errors for accidental resonance processes such as are considered here. An attempt was made by Hasted and Lee (1962) to take account of polarization and coulombic interaction, and we might proceed along similar lines. But thermal ion–atom interchange collisions differ in two respects from the medium energy charge-transfer collisions considered earlier.

(i) The inward spiralling orbits seriously modify the nuclear separations r over which the transitions take place. However, the longest time is spent at the critical separation r_c; a crude approximation might be to consider the interaction at this single separation.

(ii) The centrifugal potential $P^2/2\mu r^2$ (where P is the angular momentum of impact and μ the reduced mass) is no longer unchanged during collision, since in interchange reactions there is a change in μ.

Considering only centrifugal and polarization interactions, the defect $\Delta E(0, 0 \rightarrow 0, 0)$ which is written in equation (15), may be crudely modified as follows:

$$\Delta E(0, 0 \rightarrow 0, 0)_{r_c} = \frac{\mu_i \Delta\mu}{\mu_f} v^2 + \frac{\Delta\alpha e^2}{2r_c^4} + \Delta E(0, 0 \rightarrow 0, 0)_\infty \tag{30}$$

where

$$\Delta\mu = \mu_f - \mu_i \tag{31}$$

$$\Delta\alpha = \alpha_i - \alpha_f \tag{32}$$

and α is the polarizability of the neutral molecule; the subscripts i and f indicate respectively initial and final. To obtain this relation the collisional angular momentum is taken as

$$P = \mu v b_c \tag{33}$$

where b_c is the critical impact parameter, such that $r_c = b_c/\sqrt{2}$. The assumption is made that $v_f = \mu_i v_i/\mu_f$, i.e. that there is no conversion of internal to kinetic energy.

Consideration of the archetypal process (11) (table 2) at $T = 300$ °K shows that the first right-hand side term in equation (30) (−0·003 ev) approximately balances the second right-hand side term (+0·004 ev). The balance of centrifugal and polarization interactions results in the use of $\Delta E(0, 0 \rightarrow 0, 0)$ being unexpectedly successful. However, future calculations will no doubt include these two interactions. The rotational quantum number of the pseudo-molecule is of order $J = 80$; this is of such magnitude that at $T = 300$ °K the rotational energy of the collidant molecule contributes only marginally, even if it were to couple efficiently. At high temperatures this is no longer the case and it will be necessary to treat the problem in greater detail.

It will be seen from the comparison of our calculations with experiment for processes (1), (3), (8) and (11) that in these instances there is a significant rise in rate constant with decreasing temperature. The present 'nearest resonance' calculations are too crude to reproduce this effect; presumably potential energy surface crossings become dominant.

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