

SEMICLASSICAL EVALUATION OF THE TEMPERATURE DEPENDENCES OF SOME KINETIC CROSS SECTIONS FOR NONSPHERICAL MOLECULES*

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Received 30 March 1977

Revised manuscript received 24 May 1977

By using semiclassical (WKB) wavefunctions and the distorted wave approximation, we obtain the temperature dependences of $\sigma(0001)$ and $\sigma(02)$ appearing in the kinetic theory of transport processes of nonspherical molecules. Contributions from reorientation and energetically inelastic collisions are treated which lead to good agreement between the theoretical and experimental temperature dependences for some diatomic molecules.

Effects of a magnetic field on the transport processes of polyatomic gases (the Senftleben–Beenakker effects) have been extensively studied (for reviews, see refs. [1,2]). In recent years, a broad experimental program has been undertaken to study the temperature dependences of the various kinetic cross sections obtained from the viscomagnetic [3] and thermal conductivity [4] effects. For example the cross sections** $\sigma(02)$, $\sigma(0001)$, $\sigma(02_0)$ etc. are measured over the range of temperatures from the boiling points to room temperature for several diatomic gases. In this range, a simple T^{-n} dependence appears to be obeyed experimentally for $\sigma(02)$ and $\sigma(0001)$. However, on closer examination no such simple dependence exists for $\sigma(02)$ or $\sigma(02_0)$ although $\sigma(0001) \propto T^{-1}$. These results are of intrinsic interest since they could reveal much about the intermolecular potential and the anisotropic part in particular.

Theoretical development has been equally extensive [5–11] on the formal level. At present the theoretical problem is reduced to the level where some explicit calculations of transport cross sections are needed in order to make contact with experiment. Since such transport cross sections are given in terms of scat-

tering amplitudes [5,6,12] it is essential to calculate them by some means before their temperature dependences are calculated by averaging the scattering amplitudes with distribution functions. However, it is difficult to go beyond this step due to the classic difficulty associated with solving collision phenomena for many-particle systems. There have been some theoretical attempts made to overcome this difficulty, by assuming certain models for collision processes, but the models [8,9] used are invariably unrealistic from a physical viewpoint, being introduced often for the sake of mathematical expediency. Moreover, such models have led to incorrect temperature dependences. It is perhaps preferable to use certain approximations with more realistic physical models, provided that the range of validity is known of the approximations from other sources. In this communication we report on the results of the temperature dependences of transport (kinetic) cross sections for diatomic molecules by using semiclassical (WKB) wavefunctions to evaluate the scattering amplitudes. The emphasis is on the qualitative and physical consequences of this approach rather than on the quantitative aspects. We believe that this will shed more light on the complex dynamical processes involved than a brute force numerical method. At least the results here will hopefully be a guide to future numerical work.

In the discussion here we adopt the notations of the papers by Chen et al. [5] and Moraal [10]. The object of this work is to study the cross sections $\sigma(0001)$ and

* Supported in part by grants from the National Research Council of Canada (to BCE and BCS).

** For the notation of the kinetic cross sections, see refs. [2,5].

$\sigma(02) \equiv \sigma_{re}(02) + \sigma_{in}(02)$. Here the cross section $\sigma(02)$ is associated with the second rank tensor in the angular momentum $[J]^{(2)}$. It is composed of two parts, the cross section due to purely reorienting collisions, $\sigma_{re}(02)$ and that due to inelastic collisions, $\sigma_{in}(02)$. The cross section $\sigma(0001)$ arises from rotational relaxation. As shown in ref. [5], these cross sections can be written in terms of $\sigma_p^{(1)}$ defined by,

$$\begin{aligned} \sigma_p^{(1)}(00Ll_1l_2|\chi)_0 &\equiv \sigma_p^{(1)}(00Ll_1l_2|00Ll_1l_2|\chi)_0 \\ &= 16\pi^{5/2}\hbar^2(\pi\mu/8k_B T)^{1/2} \\ &\times \int \exp\{-\frac{1}{2}[\gamma^2 + (\gamma')^2]\} (2L+1)^{-1/2} \\ &\times A_{l_1l_2}^L(g, g') \odot^L A_{l_1l_2}^{L*}(g, g') \\ &\times \delta(\frac{1}{2}\mu(g')^2 - \frac{1}{2}\mu g^2 + \chi) d(\mu g') d\gamma': \end{aligned} \quad (1)$$

Here χ is the energy transfer between molecules 1 and 2 during a collision, $\chi = E_{j_1'j_2'} - E_{j_1j_2} \equiv -\epsilon k_B T$. The scattering amplitude $A_{l_1l_2}^L(g, g')$ is the central quantity which is obtained once the collision dynamics of non-spherical molecules is solved. For the systems of experimental interest, the dominant anisotropic couplings arise from long range forces and are generally not too strong in comparison with the spherical potential. Hence the scattering amplitude should be calculated to a good approximation by the distorted wave Born approximation. This is a commonly used approximation [5-10] which, despite the limitations which are sometimes undeservedly exaggerated, works fairly well for some scattering problems when used judiciously. The diatomic systems which have weak anisotropies, are considered here to belong to such cases. In fact for all realistic systems, even this method is impractical, being time consuming, and thus expensive, if exact solutions are sought for the distorted wavefunctions. For this reason, as mentioned above, the existing theories [8,9] have employed oversimplified potential functions which are unsatisfactory when comparison with experiment is undertaken.

The high temperature approximation is also used here [10]. Since the rotational temperatures of the molecules considered, e.g. CO and N₂, are only a few degrees Kelvin, and the experimental temperature ranges are considerably higher than these, the high temperature approximation should be reasonably accurate for treating the collision dynamics. This means

that the rotational as well as the translational motion is almost classical so that it is possible to calculate the distorted wavefunctions semiclassically by using the well known WKB method.

When the temperature is much higher than the rotational temperature, θ_{rot} , both $\sigma_{in}(02)$ and $\sigma(0001)$ are proportional to

$$T^{-1} \sigma_p^{(1)}(00Ll_1l_2|\chi), \quad \langle \chi \rangle = 2k_B(\pi\theta_{rot} T)^{1/2},$$

while $\sigma_{re}(02)$ is proportional to

$$T^{-1} \sigma_p^{(1)}(00Ll_1l_2|0)_0.$$

Following a procedure similar to Moraal's, eq. (1) can be expressed in the form,

$$\begin{aligned} \sigma_p^{(1)}(00Ll_1l_2|\chi)_0 &= (2/\pi\hbar^4)(2L+1)^{-1/2} \\ &\times \exp(\chi/2k_B T) \int_0^\infty d\gamma \gamma^2 \gamma' e^{-\gamma^2} \\ &\times \sum_{m_1, m_2} \frac{|\lambda(m_1 L m_2)|^2}{k^2(k')^2} |\beta_{l_1 l_2 L}^{m_1 m_2}(\gamma, \gamma')|^2, \end{aligned} \quad (2)$$

where

$$\begin{aligned} (\gamma')^2 &= \gamma^2 - \chi/k_B T, \\ \lambda(m_1 L m_2) &= 4\pi i^{m_1+m_2+L} [(2m_1+1)(2m_2+1)]^{1/2} \\ &\times (2L+1)^{1/2} \begin{pmatrix} m_1 & L & m_2 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (3)$$

and

$$\begin{aligned} \beta_{l_1 l_2 L}^{m_1 m_2}(\gamma \gamma') &= \int dR U_{m_1}^*(kR) b^{(l_1 l_2 L)}(R) U_{m_2}(k'R). \end{aligned} \quad (4)$$

Here we propose to use the WKB wavefunction [13] for $U_{m_j}(kR)$. By substituting the WKB wavefunctions into (4) and making use of the method of stationary phase for evaluation ‡ of the integral over R , it is possible to analyze the temperature dependence of (2) analytically. There are two different cases to consider. There are: the case when $\chi = 0$, i.e., the case of re-orientation only which is a result of intramultiplet

‡ This type of procedure has been successfully applied for collision dynamics to obtain analytic formulas of the energy dependences of cross sections. See ref. [14].

transitions without energy exchange; and the case when $\chi \neq 0$ due to energy exchange between translational and rotational degrees of freedom. If $\chi = 0$, the above procedure gives

$$\beta_{l_1 l_2 L}^{m_1 m_2} \approx \delta_{m_1 m_2} (k/2) \int_{R_1}^{\infty} dR b^{(l_1 l_2 L)}(R) / k_{m_1}(R), \quad (5)$$

where

$$k_{m_1}(R) = [k^2 - m_1(m_1 + 1)/R^2 - (2m/k^2)V_0(R)]^{1/2}.$$

$V_0(R)$ is the spherical part of the potential, which is responsible for the distortion of the unperturbed wavefunction and R_1 is the classical point. If $\chi \neq 0$, then it is found that

$$\beta_{l_1 l_2 L}^{m_1 m_2} \approx \text{Re} \left\{ \frac{1}{2} (kk')^{1/2} \frac{b^{(l_1 l_2 L)}(R_s)}{k_{m_1}(R_s)} \times \exp \left[i \int_{R_0}^{R_s} [k_{m_1}(R) - k_{m_2}(R)] dR \right] \times [\pi / |\xi''(R_s)|]^{1/2} \exp \left[\frac{1}{4} \pi i \text{sign}(\xi''(R_s)) \right] \right\}, \quad (6)$$

$$R_0 = \max(R_1, R_2).$$

Here R_s is the stationary phase point and is defined by

$$R_s = [(m_1 - m_2)(m_1 + m_2 + 1)\hbar^2 / 2\mu\chi]^{1/2},$$

while

$$\xi'' = 2\mu\chi / \hbar^2 R_s k_{m_1}(R_s).$$

Consider the integral in (5) first. Since the scattering amplitude gets a major contribution from the long range part of the anisotropic potential $b^{(l_1 l_2 L)}(R)$, the relevant orbital angular momentum m is large, and the interaction is dominantly determined by the attractive part of V_0 . Taking this into account, it is reasonable to retain the attractive long range portion of the anisotropic part, namely, $b^{(l_1 l_2 L)}$ and the spherical part, V_0 , for calculation of the integral in (5). Now assuming the following forms, $V_0 = -(\hbar^2/2\mu)uR^{-\delta}$ and $b^{(l_1 l_2 L)} = -b_0 R^{-\eta}$ and defining new variables $z = m/kR$ and $z_m = (m/k)(k^2/\delta\mu)^{1/2}$, the integral in (5) can be rewritten as

$$2\beta_{l_1 l_2 L}^{m m} = -b_0 (m/k)^{-\eta+1} \times \int_0^{z_0(z_m)} dz [1 - z^2 - \delta^{-1}(z/z_m)^\delta]^{-1/2} z^{\eta-2} \equiv -b_0 (m/k)^{-\eta+1} \chi(z_m). \quad (7)$$

After substituting this into (2), making a large m approximation, and changing the variable m to z_m , we find that the integral of $\chi(z_m)$ over m becomes independent of k . Therefore $\chi(z_m)$ is a dynamical form factor that simply appears as a constant in the temperature dependence of the transport cross section. This procedure leads to the temperature dependence of $\sigma_p^{(1)}(\chi=0)_0$, which is proportional to $T^{-1+2(\eta-2)/\delta}$ or, if $\delta = \eta$, to $T^{-4/\delta}$. If $\delta = 6$ is chosen, then

$$\sigma_p^{(1)}(0)_0 \propto T^{1/3}. \quad (8)$$

The integral for inelastic collision in (6) can be treated similarly. It is found that $\sigma_p^{(1)}(\chi \neq 0)_0$ is proportional to $T^{-1+2(\eta-2)/(\delta+2)}$ or if $\delta = \eta$, to $T^{-8/(\delta+2)}$. Again, if δ is chosen to be 6, then

$$\sigma_p^{(1)}(\chi)_0 \propto T^0. \quad (9)$$

For comparison with experiment, consider first $\sigma(0001)$ and $\sigma_{in}(02)$. Since these depend only on inelastic processes, it is found that both cross sections with $\delta = 6$ are inversely proportional to the temperature, viz.

$$\sigma(0001) \propto T^{-1}; \quad \sigma_{in}(02) \propto T^{-1}. \quad (10)$$

This temperature dependence agrees well with the experimental results for [3] N_2 and CO for $\sigma(0001)$ but the exponent is too large for $\sigma(02)$ (see fig. 1 and table

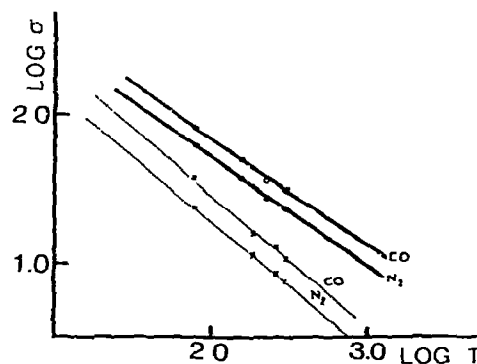


Fig. 1. Plot of $\ln(\sigma)$ versus $\ln(T)$ for the experimental values of $\sigma(0001)$ (dashed line) and $\sigma(02)$ (solid line). The units of σ and T are respectively in Å^2 and degrees Kelvin.

Table 1

Comparison of experimental and theoretical temperature dependences via the exponents obtained from the slopes in fig. 1 and from the present theory for (a) reorientation collisions [eq. (11)] and (b) inelastic collisions [eq. (10)]

n	$\sigma(0001)$		$\sigma(02)$	
	N ₂	CO	N ₂	CO
n _{exp.}	0.870	0.954	0.725	0.755
n _{theo.}	1(b)	1(b)	$\frac{2}{3}$ (a), 1(b)	$\frac{2}{3}$ (a), 1(b)

1). With the same δ , we calculate $\sigma_{re}(02)$ which is found to have the temperature dependence,

$$\sigma_{re}(02) \propto T^{-2/3} \quad (11)$$

This temperature dependence appears to be lower than the experimental value. In fact both inelastic and reorientation contributions must be combined,

$$\sigma(02) = \sigma_{in}^0(02) T^{-1} + \sigma_{re}^0 T^{-2/3}, \quad (12)$$

where the superscript 0 denotes the temperature independent contributions. The best fit of this equation to the experimental points is given in fig. 2. The values for $\sigma_{in}^0(02)$ and $\sigma_{re}^0(02)$ at various temperatures are listed in table 2. It is seen that $\sigma_{re}(02) > \sigma_{in}(02)$ as expected

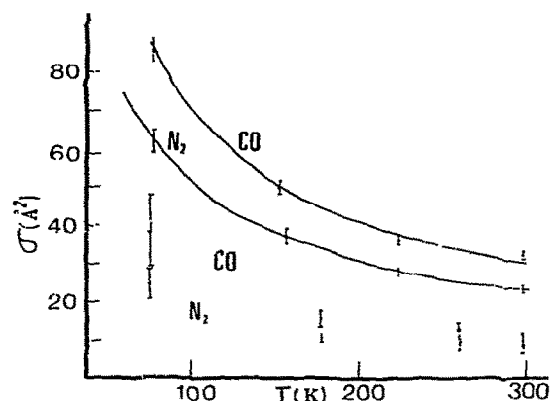


Fig. 2. Temperature dependence of $\sigma(02)$ and $\sigma(0001)$ using respectively eqs. (12) and (10) of text and the values in table 2 for N₂ and CO. Solid lines: $\sigma(02)$; dashed lines: $\sigma(0001)$.

since it is easier for diatomic molecules to reorient than exchange energy. It should indeed be possible to verify this assumption by an explicit calculation. The result above shows that the temperature dependences of reorientation and inelastic processes are mainly determined by the attractive part of the anisotropic potential for the temperature range studied here and in experiment. Moreover, since $\sigma_p^{(1)}(\chi)$ has different temperature dependences for $\chi = 0$, the commonly used "elastic approximation" $\chi = 0$, appear to be incorrect.

Table 2

Comparison of experimentally and theoretically obtained values for $\sigma(02)$ and $\sigma(0001)$ as a function of temperature for N₂ and CO

N ₂								
$\sigma_{in}^0(02) = 940 (\text{Å}^2 \text{K})$		$\sigma_{re}^0 = 905 (\text{Å}^2 \text{K}^{2/3})$			$\sigma_{in}^0(0001) = 2225 (\text{Å}^2 \text{K})$			
T	$\sigma_{in}(02)$ (Å ²)	$\sigma_{re}(02)$ (Å ²)	$\sigma(02)$ (Å ²)	$\sigma(02)(\text{Å}^2)$ (exp. [3])	T	$\sigma(0001)(\text{Å}^2)$ (theory)	$\sigma(0001)(\text{Å}^2)$ (exp. [12])	
77.3	12.1	49.7	61.8	61.9 ± 2.2	77.1	28.8	24.5 ± 4.4	
156	6.1	31.5	37.6	37.7 ± 1.9	180	12.3	11.0 ± 1.3	
223	2.9	24.6	27.5	27.8 ± 1.1	260	8.6	8.8 ± 1.1	
293	3.2	20.5	23.7	23.7 ± 0.9	293	7.6	7.6 ± 0.08	
CO								
$\sigma_{in}^0(02) = 2370 (\text{Å}^2 \text{K})$		$\sigma_{re}^0(02) = 1020 (\text{Å}^2 \text{K}^{2/3})$			$\sigma_{in}^0(0001) = 3075 (\text{Å}^2 \text{K})$			
T	$\sigma_{in}(02)$ (Å ²)	$\sigma_{re}(02)$ (Å ²)	$\sigma(02)$ (Å ²)	$\sigma(02)(\text{Å}^2)$ (exp. [3])	T	$\sigma(0001)(\text{Å}^2)$ (theory)	$\sigma(0001)(\text{Å}^2)$ (exp. [12])	
77.3	30.7	56.2	86.9	85.6 ± 3.2	77.1	39.9	38.0 ± 1.0	
154	15.4	35.5	50.9	50.1 ± 1.5	180	17.1	15.8 ± 2.5	
223	10.6	27.7	38.4	36.3 ± 1.5	260	11.8	12.5 ± 1.9	
293	8.1	23.1	31.2	32.5 ± 0.8	293	10.5	10.5 ± 1.5	

Another interesting case to which the present method should be applicable is $\sigma_{(20)}^{(02)}$ which is a measure of $[J]^{(2)}$ polarization collisionally produced from a velocity polarization, $[W]^{(2)}$. The available experimental data also show that $\sigma_{(20)}^{(02)}$ does not have a simple power law temperature dependence [3]. Within the approximations here, the only contribution to $\sigma_{(20)}^{(02)}$ arises from inelastic collisions and this has a temperature dependence of T^{-1} . The lack of agreement between this predicted value and the experimental behaviour indicates that either the repulsive part of the potential plays a dominant role or reorientation contributions which arise in the second distorted wave Born approximation should be included.

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