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ADIABATIC EXCITATION TRANSFER IN GASES: EFFECTS ON TRANSPORT

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ADIABATIC EXCITATION TRANSFER IN GASES: EFFECTS
ON TRANSPORT

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ABSTRACT

A calculation is made of the contribution to the transport coefficients from adiabatic excitation transfer in atomic gases. Atomic nitrogen is chosen as an example, and the necessary potential curves are determined partly from spectroscopic data and partly from Heitler-London calculations. Exchange greatly reduces the rate of diffusion of internal electronic energy, and the contribution of the 2D and 2P excited states of N to the thermal conductivity at $10,000^{\circ}K$ is reduced by a factor of three (from 48% to 16% of the translational thermal conductivity). Reasons are given to suppose that such behavior is fairly general, and not restricted to nitrogen.

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I. INTRODUCTION

The role of electronically excited atoms in affecting transport processes, especially at high temperatures, has often been discussed, but no quantitative calculations have been made. Hirschfelder and Eliason¹ made rough calculations of the increase in the elastic cross section, using Slater orbitals, and suggested a large effect. Mason, Vanderslice, and Yos² later suggested that the resonant exchange of excitation on collision might have an even larger effect, especially on the thermal conductivity.

The purpose of this paper is to investigate these effects in more quantitative detail, for reactions of the type



We first give a precise semiclassical formulation for the calculation of transport cross sections when both exchange and elastic scattering are important. This avoids several of the approximations of ref.2. Numerical calculations for atomic nitrogen show that the diffusion of electronically excited atoms is rather slow, and that the maximum contribution of the electronic excitation to the thermal conductivity is small (<20%).

Arguments are advanced to show that this result is probably valid for most systems, not just nitrogen.

If inelastic collisions occur frequently enough to keep the gas in local equilibrium, the thermal conductivity λ is^{3,4}

$$\lambda = \lambda_{\text{trans}} + \lambda_{\text{int}} = \frac{5}{2} \eta \bar{c}_{\text{trans}} + \rho D_{\text{int}} \bar{c}_{\text{int}}, \quad (2)$$

where η is the viscosity, \bar{c}_{trans} the translational specific heat, ρ the mass density, D_{int} the diffusion coefficient for internal energy, and \bar{c}_{int} the specific heat for the internal degrees of freedom. If the inelastic collisions are too infrequent to maintain local equilibrium, the heat conduction is lowered.⁵

If the inelastic collisions are so frequent that the translational distribution function is perturbed, the heat conduction is also lowered.⁶ Since $\bar{c}_{\text{trans}} = \frac{3}{2} k/m$, Eq.(2) can be written as

$$\frac{\lambda_m}{\eta k} = \frac{15}{4} + \frac{\rho D_{\text{int}}}{\eta} \frac{C_{\text{int}}}{k}, \quad (3)$$

where k is Boltzmann's constant and C_{int} is the internal heat capacity per molecule. From this it follows that the contribution to the thermal conductivity from the internal degrees of freedom has importance only where C_{int} is large. The maximum electronic contribution to C_{int}/k is usually less than unity,⁷ and $\rho D_{\text{int}}/\eta$ is of order unity without excitation exchange. The maximum contribution of electronic excitation to λ is thus never very large, and exchange reduces it by decreasing D_{int} .

II. CROSS SECTIONS

For symmetric exchange reactions like Eq.(1) there exists a simple approximate relation between the diffusion cross section Q_D and the exchange cross section Q_{ex} . An exact statement about this relation is given in Appendix A. Here we give a simple physical derivation of the equation, based on the semiclassical assumption that the nuclei follow trajectories which are

independent of a possible excitation exchange that takes place with probability P_{ex} . The only effect of exchange is to convert the apparent classical deflection angle from θ to $\pi - \theta$, just as in charge transfer,⁸ so that

$$\begin{aligned} Q_D &= Q_D(\text{without exchange}) + Q_D(\text{with exchange}) \\ &= 2\pi \int_0^\infty (1 - P_{\text{ex}}) (1 - \cos \theta) b db \\ &\quad + 2\pi \int_0^\infty P_{\text{ex}} [1 - \cos(\pi - \theta)] b db, \end{aligned} \quad (4)$$

where b is the impact parameter. This expression can be rearranged into the form

$$Q_D = 4\pi \int_0^\infty P_{\text{ex}} b db + 2\pi \int_0^\infty (1 - 2P_{\text{ex}}) (1 - \cos \theta) b db. \quad (5)$$

Here the first term is equal to $2Q_{\text{ex}}$, and the last term is generally negligible because $P_{\text{ex}} \approx 1/2$ for small impact parameters (on the average) and $\cos \theta \approx 1$ for large impact parameters. When this is not true the full expressions in Appendix A should be used, but in such cases exchange is usually not important anyway. In the following we will therefore use the simple relation, $Q_D \approx 2Q_{\text{ex}}$, transforming calculations of diffusion cross sections into calculations of exchange cross sections.

In the adiabatic approximation a collision between two atoms of the same kind but in different electronic states involves coupling between two potential curves, one for which the molecular wave function is symmetric (gerade) and one for which it is

antisymmetric (ungerade). If both atoms are in S-states there is only one possible pair of potential curves, and the calculation of Q_{ex} in terms of the elastic scattering phase shifts is well known.⁹ If both atoms are not in S-states, there are possibilities for a number of pairs of potential curves.¹⁰ In the adiabatic approximation there is no coupling between different pairs of such potential curves, and a simple average over all pairs can be used,²

$$\langle Q_{\text{ex}} \rangle = \sum_n p_n Q_{\text{ex}}^{(n)}, \quad (5)$$

where p_n is the probability that a collision will follow the n -th pair of potential curves. The p_n are easily calculated from the statistical weights of the molecular states.

For the present purposes an impact-parameter calculation of Q_{ex} should be sufficiently accurate, for which

$$Q_{\text{ex}}^{(n)} = 2\pi \int_0^\infty \sin^2 \zeta_n b db, \quad (6)$$

$$\zeta_n = \frac{1}{\hbar v} \int_b^\infty \frac{|\varphi_g^{(n)} - \varphi_u^{(n)}|}{(r^2 - b^2)^{\frac{1}{2}}} r dr, \quad (7)$$

where v is the relative velocity of collision and $\varphi_g^{(n)}$ and $\varphi_u^{(n)}$ are the n -th pair of potential curves. It usually happens that the difference between the two potential curves can be satisfactorily fitted by an exponential,

$$|\varphi_g^{(n)} - \varphi_u^{(n)}| = A_n \exp(-\alpha_n r), \quad (8)$$

where A_n and α_n are constants. In this case Firsov's approximation¹¹ can be used to evaluate the integrals in Eqs.(6) and (7), yielding

$$Q_{\text{ex}}^{(n)} = \frac{1}{2} \pi \left[b_c^{(n)} \right]^2, \quad (9)$$

where $b_c^{(n)}$ is given by a transcendental equation,

$$\frac{A_n}{\hbar v} \left[\frac{\pi b_c^{(n)}}{2 \alpha_n} \right]^{\frac{1}{2}} \exp \left[-\alpha_n b_c^{(n)} \right] = \frac{1}{\pi}. \quad (10)$$

Bates and Boyd¹² have shown that this simple approximation is remarkably accurate.

Thus the calculation of $Q_{\text{ex}}^{(n)}$ is simple once the potential difference is given in the form of the parameters A_n and α_n . The energy dependence of $Q_{\text{ex}}^{(n)}$ is fairly weak and can be expressed as¹³

$$Q_{\text{ex}}^{(n)} = \left[c_1^{(n)} - c_2^{(n)} \ln v \right]^2, \quad (11)$$

where $c_1^{(n)}$ and $c_2^{(n)}$ are constants.

III. THERMAL CONDUCTIVITY AND INTERNAL DIFFUSION

The expression for the diffusion coefficient from the kinetic theory of gases can be written in the form¹⁴

$$\rho D = \frac{3}{8} \frac{(2\pi\mu kT)^{\frac{1}{2}}}{\pi \bar{\Omega}(1,1)}, \quad (12)$$

where

$$\pi \bar{\Omega}(1,1) = \int_0^\infty Q_D \gamma^5 e^{-\gamma^2} d\gamma, \quad (13)$$

in which $\gamma^2 = \mu v^2 / 2kT$ and μ is the reduced mass. When exchange dominates and $Q_D \approx 2Q_{\text{ex}}$, Eq.(12) still holds with the replacement

$$\pi \bar{\Omega}^{(1,1)} = 2\pi \sum_n p_n \Omega_{\text{ex}}^{(n)} = 2 \sum_n p_n \int_0^\infty Q_{\text{ex}}^{(n)} \gamma^5 e^{-\gamma^2} d\gamma. \quad (14)$$

This integral is easily evaluated when $Q_{\text{ex}}^{(n)}$ has the energy dependence of Eq.(11).¹⁵

The viscosity of a gas with not too many excited atoms can be taken approximately equal to the viscosity of the ground-state gas, which is¹⁴

$$\eta = \frac{5}{16} \frac{(2\pi\mu kT)^{\frac{1}{2}}}{\pi \bar{\Omega}^{(2,2)}}, \quad (15)$$

where $\bar{\Omega}^{(2,2)}$ is the collision integral for viscosity. Combining the foregoing equations, we obtain

$$\frac{\lambda_m}{\eta k} = \frac{15}{4} + \frac{3}{5} \frac{C_{\text{int}}}{k} \frac{\bar{\Omega}^{(2,2)}}{\sum_n p_n \Omega_{\text{ex}}^{(n)}}. \quad (16)$$

The contribution to C_{int} from an excited electronic state of energy ΔE above the ground state is

$$\frac{C_{\text{int}}}{k} = \frac{(\Delta E/kT)^2 \omega \exp(-\Delta E/kT)}{\left[1 + \omega \exp(-\Delta E/kT)\right]^2}, \quad (17)$$

where ω is the ratio of the degeneracy of the excited state to that of the ground state.

Abnormalities in the thermal conductivity should be especially pronounced in systems that have low-lying excited states. As a numerical example we select atomic nitrogen, since the results are of some practical interest for their own sake. The following data are from Herzberg.¹⁰ The ground state is 4S , with an excited 2D state 2.38 eV above and an excited 2P state

3.65 eV above. In collisions between $N(^4S)$ and $N(^2D)$ the following (g,u)-pairs of potential curves are possible: $^3\Sigma_{g,u}$, $^5\Sigma_{g,u}$, $^3\Pi_{g,u}$, $^5\Pi_{g,u}$, $^3\Delta_{g,u}$, and $^5\Delta_{g,u}$. In collisions between $N(^4S)$ and $N(^2P)$ the first four of these pairs are possible. The degeneracies are as shown in Tables I and II.

In the calculation we need the constants A_n and α_n of Eq.(8) for the different (g,u)-pairs of potentials. A direct way to determine these constants is to fit potential curves determined from spectroscopic data, but unfortunately such information is available for only a few of the needed states, namely $^3\Pi_g$ and $^3\Pi_u$ for $N(^4S) + N(^2D)$ and $^3\Sigma_u$ for $N(^4S) + N(^2P)$.¹⁶ Lacking direct information on the potentials, we turn to quantum-mechanical calculations. In the next section a calculation of the potential curves of interest is carried out with the Heitler-London approximation, and it is shown that the following simple relations among the energies of different states can be obtained by the introduction of a reasonable assumption:

$$\left| ^5\Sigma_g - ^5\Sigma_u \right| = 3 \left| ^3\Sigma_g - ^3\Sigma_u \right|, \quad (18a)$$

$$\left| ^5\Pi_g - ^5\Pi_u \right| = (3^{\frac{1}{2}} - 1) \left| ^3\Pi_g - ^3\Pi_u \right|, \quad (18b)$$

$$\left| ^5\Delta_g - ^5\Delta_u \right| = \frac{3}{2} \left| ^3\Delta_g - ^3\Delta_u \right|. \quad (18c)$$

Since only $\left| ^3\Pi_g - ^3\Pi_u \right|$ for the $N(^4S) + N(^2D)$ interaction is known from spectroscopic data, we make the following rough approximation in order to obtain numerical results:

$$\left| ^3\Sigma_g - ^3\Sigma_u \right| \approx \left| ^3\Pi_g - ^3\Pi_u \right| \approx \left| ^3\Delta_g - ^3\Delta_u \right|. \quad (19)$$

This suffices for the 2D state calculations. For the $N(^4S) + N(^2P)$ interactions we use the potential for the $^3\Sigma_u$ state from ref.16 and set the potential for the $^3\Sigma_g$ state equal to zero. This, together with Eqs.(18) and (19), suffices for the 2P state calculations.

The results of the calculation are given in Tables I and II for 10,000°K. This is the temperature at which C_{int}/k for the 2D state is nearly a maximum. Taking these values of $\bar{\Omega}(1,1)$ and combining them with the value of $\bar{\Omega}(2,2)$ for N atoms,¹⁷ we find $\rho D_{int}/\eta$ to be 0.54 for the 2D state and 0.30 for the 2P state, leading to an increase in λ by a factor of 1.16. Had we neglected exchange and assumed the diffusion coefficients of the excited atoms to be about the same as for ground-state atoms, we would have obtained $\rho D_{int}/\eta = 1.40$, leading to an increase in λ by a factor of 1.48.

IV. HEITLER-LONDON INTERACTION POTENTIALS

As shown by Yos,¹⁸ the wave function for a molecular state between two atoms of the same kind, but originally in different states, can approximately be written in the form

$$\Psi_{g,u}(S, M_S, L, M_L) = 2^{-\frac{1}{2}} \left[\Psi_A(S, M_S, M_{L_A}, M_{L_B}) \pm \Psi_B(S, M_S, M_{L_B}, M_{L_A}) \right], \quad (20)$$

where

$$\begin{aligned} \Psi_A(S, M_S, M_{L_A}, M_{L_B}) = & \\ & \sum_{\substack{M_{S_A} + M_{S_B} = M_S \\ M_{S_A}, M_{S_B}}} C(M_{S_A}, M_{S_B}; S, M_S) \Psi_A(M_{L_A}, M_{S_A}) \Psi_B(M_{L_B}, M_{S_B}), \quad (21) \end{aligned}$$

with a similar expression for Ψ_B . Here $C(M_{S_A}, M_{S_B}; S, M_S)$ are the Clebsch-Gordan coefficients, which can be readily evaluated in specific cases from Table 20-5 of Slater,¹⁹ $\psi_A(M_{L_A}, M_{S_A})$ and $\psi_B'(M_{L_B}, M_{S_B})$ are Hartree-Fock wave functions for the isolated atoms as described by the indicated quantum numbers, and \hat{A} is an operator that antisymmetrizes the product of the partially antisymmetrized atomic wave functions ψ_A and ψ_B' . As these are given as sums of Slater determinants this operation involves, as mentioned by Yos, simply a substitution of the product of Slater determinants each of order N by one Slater determinant of order $2N$ having the same one-electron wave functions.

The determination of the atomic wave functions with proper symmetry is treated for instance in ref.19. The results can be read from Table A11-5 of Slater²⁰ for the cases of interest here: $N(4S)$, $N(2D)$, and $N(2P)$, all of the configuration p^3 . Hartree-Fock solutions for the radial wave functions are available for these states,²¹ but we will give here only a formal treatment. This is sufficient to obtain approximate relations among the different molecular states, in which we are especially interested. Following a method which is essentially the same as the LCAO treatment of the H_2^+ problem, we obtain from Eq.(20) the result

$$\varphi_g - \varphi_u \approx 2H_{AB}/S_{AA}, \quad (22)$$

where

$$H_{AB} = \int \Psi_A H \Psi_B d\tau, \quad (23)$$

and the overlap integral S_{AB} has been neglected since we are interested in the results for large interatomic separations.

It is now easy to show (Appendix B) that the matrix elements can be written in the form

$$H_{AB}(S, \Lambda) = \sum_{\tau} (-1)^{\tau} a(S, \Lambda; \tau_1 \cdots \tau_6) K(\Lambda; \tau_1 \cdots \tau_6), \quad (24)$$

where S and Λ are quantum numbers for the molecular states. The summation is over all permutations between all electrons, of which only the coordinates for the electrons from the unfilled shells are shown explicitly. τ is the perturbation number. The spin factors a and the exchange integrals K are given in Tables III and IV for molecular states between $N(^4S)$ and $N(^2D)$. In a first approximation the summation in Eq.(24) can be restricted to the terms in which only one pair of electrons from the unfilled shells have been exchanged between the atoms.¹⁸ If we make the further restriction that only those terms are retained in which the electrons which are not exchanged between atoms remain in their original one-electron orbitals,²² we are able to find simple relations among different states of the same Λ . With these restrictions we get for $N(^4S) + N(^2D)$ only the few terms listed in Table V.

For the terms listed in Table V, a simple proportionality among the a 's is found for the Σ states, all K_1 and all K_2 exchange integrals are equal for the Π states, and all $K(2)$ integrals are equal for the Δ states. As a result, we obtain the relations between different molecular states given in Eqs.(18).

In the same way it can be shown that the first two relations of Eqs.(18) also hold for the molecular states between $N(^4S)$ and $N(^2P)$.

V. DISCUSSION

Although the lack of information on the potential curves limits the accuracy of the detailed calculations, we believe that a few general conclusions are possible. First of all, the maximum possible contribution of an electronically excited state to the thermal conductivity is never very large, although it is not necessarily small. It is probably always less than half of the translational energy contribution. Hirschfelder²³ reached this conclusion some time ago; our calculations merely supply additional quantitative evidence. Secondly, the influence of resonant excitation exchange collisions on the thermal conductivity is quite important. Our calculations indicate a reduction in λ_{int} by about a factor of three for N atoms at 10,000°K because of exchange. In short, for many cases of interest the contribution of λ_{int} is probably small but not negligible.

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APPENDIX A. TRANSPORT CROSS SECTIONS WITH EXCHANGE

The differential cross section $I(\theta)$ for collisions of the type $A^* + A \rightarrow A + A^*$ involving only one pair of potential curves has been shown by Massey and Smith²⁴ to be

$$I^\pm(\theta) = \frac{1}{4} \left| f_g(\theta) + f_u(\theta) \pm [f_g(\pi-\theta) - f_u(\pi-\theta)] \right|^2, \quad (A1)$$

where \underline{g} and \underline{u} refer to the gerade and ungerade potentials, respectively. When more than one pair of potentials is involved, a simple statistical average of $I(\theta)$ over all pairs can be used.² The + sign in Eq.(A1) is used for atoms with total spin even, and the - sign for atoms with total spin odd. As usual the scattering amplitudes $f(\theta)$ are given in terms of the phase shifts η_ℓ by

$$f_{g,u}(\theta) = (2ik)^{-1} \sum_{\ell} (2\ell+1) \left[\exp(2i\eta_\ell^{g,u}) - 1 \right] P_\ell(\cos \theta). \quad (A2)$$

If we define diffusion cross sections for hypothetical atoms of zero nuclear spin as

$$Q_D^\pm = 2\pi \int_0^\pi (1 - \cos \theta) I^\pm(\theta) \sin \theta d\theta, \quad (A3)$$

then the diffusion cross sections for atoms of nuclear spin \underline{s} are

$$\begin{aligned} Q_D \left(\begin{array}{c} \text{BE} \\ \text{FD} \end{array} \right) &= \left(\frac{s+1}{2s+1} \right) Q_D^\pm + \left(\frac{s}{2s+1} \right) Q_D^\mp, \\ &= \frac{1}{2} (Q_D^+ + Q_D^-) \pm \frac{1}{2(2s+1)} (Q_D^+ - Q_D^-), \end{aligned} \quad (A4)$$

depending on whether the atoms follow Bose-Einstein or Fermi-Dirac statistics. Combining Eqs.(A1)-(A3), we obtain

$$Q_D^{\pm} = \frac{4\pi}{k^2} \sum_{\substack{\text{even} \\ \text{odd}}} (\ell + 1) \sin^2 \left(\eta_{\ell}^g - \eta_{\ell+1}^u \right) + \frac{4\pi}{k^2} \sum_{\substack{\text{odd} \\ \text{even}}} (\ell + 1) \sin^2 \left(\eta_{\ell}^u - \eta_{\ell+1}^g \right) . \quad (A5)$$

Similar results hold for the exchange cross section,²⁴

$$I_{\text{ex}}(\theta) = \frac{1}{4} \left| f_g(\pi - \theta) - f_u(\pi - \theta) \right|^2 , \quad (A6)$$

$$Q_{\text{ex}} = 2\pi \int_0^{\pi} I_{\text{ex}}(\theta) \sin \theta d\theta , \quad (A7)$$

from which follows

$$Q_{\text{ex}} = \frac{\pi}{k^2} \sum (2\ell + 1) \sin^2(\eta_{\ell}^g - \eta_{\ell}^u) . \quad (A8)$$

It is convenient to pass to the semiclassical limit at this point, in which it is assumed that many phase shifts contribute to Q_D and Q_{ex} . In particular, the sums over ℓ are replaced by integrals, and the differences between phase shifts are replaced by derivatives,

$$\eta_{\ell+1}^{g,u} - \eta_{\ell}^{g,u} = \frac{d\eta_{\ell}^{g,u}}{d\ell} . \quad (A9)$$

It is further assumed that the phase shifts are given sufficiently accurately by the JWKB approximation. This relates the phase shifts and the classical deflection angles,

$$\theta = 2d\eta_{\ell}/d\ell . \quad (A10)$$

Taking the impact parameter as $bk = (\ell + \frac{1}{2})$, and carrying out some straightforward manipulations, we obtain

$$Q_{\text{ex}} = 2\pi \int_0^{\infty} P_{\text{ex}} b db , \quad (A11)$$

where

$$P_{\text{ex}} = \sin^2(\eta_\ell^g - \eta_\ell^u) , \quad (\text{A12})$$

$$\begin{aligned} \eta_\ell^g - \eta_\ell^u \equiv \zeta(b) &= k \int_{r_g}^{\infty} \left[1 - \left(\frac{b}{r} \right)^2 - \frac{2\varphi_g}{\mu v^2} \right]^{\frac{1}{2}} dr \\ &\quad - k \int_{r_u}^{\infty} \left[1 - \left(\frac{b}{r} \right)^2 - \frac{2\varphi_u}{\mu v^2} \right]^{\frac{1}{2}} dr , \end{aligned} \quad (\text{A13})$$

in which r_g and r_u are the distances of closest approach for the φ_g and φ_u potentials. If we take $r_g = r_u = b$ and carry out a binomial expansion of the integrands in Eq.(A13), we obtain Eq.(7) as the leading term. We also obtain for Q_D , after carrying out some trigonometric transformations,

$$Q_D \begin{pmatrix} \text{BE} \\ \text{FD} \end{pmatrix} = Q_D (\text{class}) \pm \frac{1}{2s+1} Q_D (\text{interfer}), \quad (\text{A14})$$

where

$$\begin{aligned} Q_D (\text{class}) &= 2Q_{\text{ex}} + \pi \int_0^{\infty} (1 - 2P_{\text{ex}}) (1 - \cos \theta_g) b db \\ &\quad + \pi \int_0^{\infty} (1 - 2P_{\text{ex}}) (1 - \cos \theta_u) b db , \end{aligned} \quad (\text{A15})$$

$$Q_D (\text{interfer}) = 2\pi \int_0^{\infty} \left[P_{\text{ex}} (1 - P_{\text{ex}}) \right]^{\frac{1}{2}} (\sin \theta_g - \sin \theta_u) b db, \quad (\text{A16})$$

and θ_g and θ_u are the classical deflection angles for the φ_g and φ_u potentials. If we take $\theta_g \approx \theta_u$ we obtain Eq.(5).

APPENDIX B. MOLECULAR WAVE FUNCTIONS FROM $N(^4S) + N(^2D)$

From Eq.(21) and from Table 20-5 of ref.19 we obtain

$$^3\Sigma (M_S=1): \Psi_A = A \left\{ \frac{\sqrt{3}}{2} \psi_A(0, \frac{3}{2}) \psi_B'(0, -\frac{1}{2}) - \frac{1}{2} \psi_A(0, \frac{1}{2}) \psi_B'(0, \frac{1}{2}) \right\} , \quad (B1)$$

$$^5\Sigma (M_S=2): \Psi_A = A \left\{ \psi_A(0, \frac{3}{2}) \psi_B'(0, \frac{1}{2}) \right\} , \quad (B2)$$

$$^3\Pi (M_S=1): \Psi_A = A \left\{ \frac{\sqrt{3}}{2} \psi_A(0, \frac{3}{2}) \psi_B'(1, -\frac{1}{2}) - \frac{1}{2} \psi_A(0, \frac{1}{2}) \psi_B'(1, \frac{1}{2}) \right\} , \quad (B3)$$

$$^5\Pi (M_S=2): \Psi_A = A \left\{ \psi_A(0, \frac{3}{2}) \psi_B'(1, \frac{1}{2}) \right\} , \quad (B4)$$

$$^3\Delta (M_S=1): \Psi_A = A \left\{ \frac{\sqrt{3}}{2} \psi_A(0, \frac{3}{2}) \psi_B'(2, -\frac{1}{2}) - \frac{1}{2} \psi_A(0, \frac{1}{2}) \psi_B'(2, \frac{1}{2}) \right\} , \quad (B5)$$

$$^5\Delta (M_S=2): \Psi_A = A \left\{ \psi_A(0, \frac{3}{2}) \psi_B'(2, \frac{1}{2}) \right\} . \quad (B6)$$

The atomic wave functions can now be taken from Table A11-5 of ref.20. Using the same notation as ref.20 with the exception that the spin part has been factored out [e.g., $(1^+ 0^- -1^+) = (\alpha\beta\alpha)(10-1)$], we obtain

$$\begin{aligned} ^3\Sigma: \Psi_A = A \left\{ \sqrt{\frac{1}{8}} (\alpha\alpha\alpha)_A \left[-(\alpha\beta\beta)_B - (\beta\beta\alpha)_B + 2(\beta\alpha\beta)_B \right] \right. \\ \left. - \sqrt{\frac{1}{72}} \left[(\alpha\alpha\beta)_A + (\beta\alpha\alpha)_A + (\alpha\beta\alpha)_A \right] \left[(\alpha\alpha\beta)_B + (\alpha\beta\beta)_B - 2(\alpha\beta\alpha)_B \right] \right\} \\ \times (10-1)_A (10-1)_B , \end{aligned} \quad (B7)$$

$${}^5\Sigma: \Psi_A = \mathbb{A} \sqrt{\frac{1}{6}} (\alpha\alpha\alpha)_A \left[(\alpha\alpha\beta)_B + (\beta\alpha\alpha)_B - 2(\alpha\beta\alpha)_B \right] \\ \times (10-1)_A (10-1)_B, \quad (\text{B8})$$

$${}^3\Pi: \Psi_A = \mathbb{A} \left\{ \sqrt{\frac{3}{8}} (\alpha\alpha\alpha)_A (\beta\alpha\beta)_B - \sqrt{\frac{1}{24}} \left[(\alpha\alpha\beta)_A + (\beta\alpha\alpha)_A + (\alpha\beta\alpha)_A \right] (\alpha\beta\alpha)_B \right\} \\ \times (10-1)_A \left[(100)_B - (11-1)_B \right], \quad (\text{B9})$$

$${}^5\Pi: \Psi_A = \mathbb{A} \sqrt{\frac{1}{2}} (\alpha\alpha\alpha)_A (\alpha\beta\alpha)_B (10-1)_A \left[(100)_B - (11-1)_B \right], \quad (\text{B10})$$

$${}^3\Delta: \Psi_A = \mathbb{A} \left\{ -\sqrt{\frac{3}{4}} (\alpha\alpha\alpha)_A (\alpha\beta\beta)_B + \sqrt{\frac{1}{12}} \left[(\alpha\alpha\beta)_A + (\beta\alpha\alpha)_A + (\alpha\beta\alpha)_A \right] (\alpha\beta\alpha)_B \right\} \\ \times (10-1)_A (110)_B, \quad (\text{B11})$$

$${}^5\Delta: \Psi_A = \mathbb{A} \left\{ -(\alpha\alpha\alpha)_A (\alpha\beta\alpha)_B \right\} (10-1)_A (110)_B. \quad (\text{B12})$$

The spin factors a and exchange integrals K then follow from application of Eq.(23).

Table I. Excitation transfer and thermal conductivity in $N(^2D) + N(^4S)$ at $10,000^\circ K$. $\Delta E = 2.38$ eV, $\omega = 10/4$, $C_{int}/k = 0.900$.

States	Stat. Weight	A_n (eV)	α_n (\AA^{-1})	$\pi\Omega_{ex}^{(n)}$ (\AA^2)
$^3\Sigma_{g,u}$	3/40	2320	4.56	12.4
$^5\Sigma_{g,u}$	5/40	6960	4.56	15.0
$^3\Pi_{g,u}$	6/40	2320	4.56	12.4
$^5\Pi_{g,u}$	10/40	1700	4.56	11.8
$^3\Delta_{g,u}$	6/40	2320	4.56	12.4
$^5\Delta_{g,u}$	10/40	3480	4.56	13.1

$$\pi\bar{\Omega}^{(1,1)} = 25.5 \text{ \AA}^2; \quad \lambda m/\eta k = 3.75 + 0.49$$

Table II. Excitation transfer and thermal conductivity in $N(^2P) + N(^4S)$ at $10,000^\circ\text{K}$. $\Delta E = 3.65 \text{ eV}$, $\omega = 6/4$, $C_{\text{int}}/k = 0.372$.

States	Stat. Weight	A_n (eV)	α_n (\AA^{-1})	$\pi_{\Omega \text{ ex}}^{(n)}$ (\AA^2)
$^3\Sigma_{g,u}$	3/24	250	2.88	22.8
$^5\Sigma_{g,u}$	5/24	750	2.88	27.6
$^3\Pi_{g,u}$	6/24	250	2.88	22.8
$^5\Pi_{g,u}$	10/24	183	2.88	21.4

$$\pi_{\Omega}^{-}(1,1) = 46.4 \text{ \AA}^2; \quad \lambda_m/\eta k = 3.75 + 0.11$$

Table III. Spin factors for molecular states from $N(^4S) + N(^2D)$.

$$^3\Sigma. \quad a = \frac{1}{8} \sum_{\text{spins}} \{ \alpha(\tau_1) \alpha(\tau_2) \alpha(\tau_3) [-\alpha(\tau_4) \beta(\tau_5) \beta(\tau_6) - \beta(\tau_4) \beta(\tau_5) \alpha(\tau_6) + 2\beta(\tau_4) \alpha(\tau_5) \beta(\tau_6)]$$

$$- \frac{1}{3} [\alpha(\tau_1) \alpha(\tau_2) \beta(\tau_3) + \beta(\tau_1) \alpha(\tau_2) \alpha(\tau_3) + \alpha(\tau_1) \beta(\tau_2) \alpha(\tau_3)] [\alpha(\tau_4) \alpha(\tau_5) \beta(\tau_6) + \beta(\tau_4) \alpha(\tau_5) \alpha(\tau_6) - 2\alpha(\tau_4) \beta(\tau_5) \alpha(\tau_6)] \{ \alpha(1) \alpha(2) \beta(3) [-\alpha(4) \beta(5) \beta(6) - \beta(4) \beta(5) \alpha(6) + 2\beta(4) \alpha(5) \beta(6)] \\ - \frac{1}{3} [\alpha(1) \alpha(2) \beta(3) + \beta(1) \alpha(2) \alpha(3) + \alpha(1) \beta(2) \alpha(3)] [\alpha(4) \alpha(5) \beta(6) + \beta(4) \alpha(5) \alpha(6) - 2\alpha(4) \beta(5) \alpha(6)] \}$$

$$^5\Sigma. \quad a = \frac{1}{6} \sum_{\text{spins}} \{ \alpha(\tau_1) \alpha(\tau_2) \alpha(\tau_3) [\alpha(\tau_4) \alpha(\tau_5) \beta(\tau_6) + \beta(\tau_4) \alpha(\tau_5) \alpha(\tau_6) - 2\alpha(\tau_4) \beta(\tau_5) \alpha(\tau_6)] \} \\ \times \{ \alpha(1) \alpha(2) \alpha(3) [\alpha(4) \alpha(5) \beta(6) + \beta(4) \alpha(5) \alpha(6) - 2\alpha(4) \beta(5) \alpha(6)] \}$$

$$^3\Pi. \quad a = \frac{3}{8} \sum_{\text{spins}} \{ \alpha(\tau_1) \alpha(\tau_2) \alpha(\tau_3) \beta(\tau_4) \alpha(\tau_5) \beta(\tau_6) - \left[\frac{1}{3} \right] [\alpha(\tau_1) \alpha(\tau_2) \beta(\tau_3) + \alpha(\tau_1) \beta(\tau_2) \alpha(\tau_3) + \alpha(\tau_1) \alpha(2) \beta(3) + \alpha(1) \beta(2) \alpha(3) + \beta(1) \alpha(2) \alpha(3)] \alpha(4) \beta(5) \alpha(6) \}$$

$$^5\Pi. \quad a = \frac{1}{2} \sum_{\text{spins}} \{ \alpha(\tau_1) \alpha(\tau_2) \alpha(\tau_3) \alpha(\tau_4) \beta(\tau_5) \alpha(\tau_6) \} \{ \alpha(1) \alpha(2) \alpha(3) \alpha(4) \beta(5) \alpha(6) \}$$

$$^3\Delta. \quad a = \frac{3}{4} \sum_{\text{spins}} \{ \alpha(\tau_1) \alpha(\tau_2) \alpha(\tau_3) \alpha(\tau_4) \beta(\tau_5) \beta(\tau_6) + \frac{1}{3} [\alpha(\tau_1) \alpha(\tau_2) \beta(\tau_3) + \beta(\tau_1) \alpha(\tau_2) \alpha(\tau_3) + \alpha(\tau_1) \beta(\tau_2) \alpha(\tau_3)] \alpha(4) \beta(5) \alpha(6) \}$$

$$^5\Delta. \quad a = \sum_{\text{spins}} \{ \alpha(\tau_1) \alpha(\tau_2) \alpha(\tau_3) \alpha(\tau_4) \beta(\tau_5) \alpha(\tau_6) \} \{ \alpha(1) \alpha(2) \alpha(3) \alpha(4) \beta(5) \alpha(6) \}$$

Table IV. Exchange integrals in terms of p_6 and p_π atomic orbitals.

$$\Sigma \text{ states: } K(0) = \int [1_B(\tau_1)0_B(\tau_2)-1_B(\tau_3)1_A(\tau_4)0_A(\tau_5)-1_A(\tau_6)] H[1_A(1)0_A(2)-1_A(3)1_B(4)0_B(5)-1_B(6)] d\tau$$

$$\Pi \text{ states: } K(1) = K_1(1)+K_2(1)-K_3(1)-K_4(1), \text{ where}$$

$$K_1(1) = \int [1_B(\tau_1)0_B(\tau_2)-1_B(\tau_3)1_A(\tau_4)0_A(\tau_5)0_A(\tau_6)] H[1_A(1)0_A(2)-1_A(3)1_B(4)0_B(5)0_B(6)] d\tau$$

$$K_2(1) = \int [1_B(\tau_1)0_B(\tau_2)-1_B(\tau_3)1_A(\tau_4)1_A(\tau_5)-1_A(\tau_6)] H[1_A(1)0_A(2)-1_A(3)1_B(4)1_B(5)-1_B(6)] d\tau$$

$$K_3(1) = \int [1_B(\tau_1)0_B(\tau_2)-1_B(\tau_3)1_A(\tau_4)0_A(\tau_5)0_A(\tau_6)] H[1_A(1)0_A(2)-1_A(3)1_B(4)1_B(5)-1_B(6)] d\tau$$

$$K_4(1) = \int [1_B(\tau_1)0_B(\tau_2)-1_B(\tau_3)1_A(\tau_4)1_A(\tau_5)-1_A(\tau_6)] H[1_A(1)0_A(2)-1_A(3)1_B(4)0_B(5)0_B(6)] d\tau$$

$$\Delta \text{ states: } K(2) = \int [1_B(\tau_1)0_B(\tau_2)-1_B(\tau_3)1_A(\tau_4)1_A(\tau_5)0_A(\tau_6)] H[1_A(1)0_A(2)-1_A(3)1_B(4)1_B(5)0_B(6)] d\tau$$

Table V. Terms different from zero in the
single-exchange approximation

	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ	$a(S=1)$	$a(S=2)$
Σ states:	1	5	6	4	2	3	2	- 1/18	1/6
	4	2	6	1	5	3	2	- 4/18	4/6
	4	5	3	1	2	6	2	- 1/18	1/6
Π states: K_3 and K_4 yield no terms in this approximation.									
K_1	4	5	3	1	2	6	2	1/8	0
	4	5	3	1	6	2	3	$-\sqrt{3}/8$	0
	4	6	3	1	2	5	3	$-\sqrt{3}/8$	0
	4	6	3	1	5	2	2	1/8	1/2
K_2	4	2	6	1	5	3	2	1/8	1/2
	4	2	6	5	1	3	3	$-\sqrt{3}/8$	0
	5	2	6	1	4	3	3	$-\sqrt{3}/8$	0
	5	2	6	4	1	3	2	1/8	0
Δ states:	4	6	3	1	5	2	2	7/12	1
	4	6	3	5	1	2	3	0	0
	5	6	3	1	4	2	3	0	0
	5	6	3	4	1	2	2	1/12	0

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