Principal Energy Transfer Pathways in the Collision of $N_2O(00^01)$ with Toluene-d_8. A (WKB) Semiclassical Study

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Vibrational energy transfer from $N_2O(00^01)$ to deuterated toluene has been studied by use of the Wentzel−Kramers−Brillouin (WKB) semiclassical procedure in the distorted-wave approximation in the temperature range of 100−500 K. Energy transfer to the CD stretch modes (ν_a'' and ν_a') on the methyl group of $C_6D_5CD_3$ is shown to be the principal pathway occurring through long-range interactions. The energy transfer to the CD stretch modes (ν_7, ν_{20}, and ν_2) on the benzene ring are found to be of minor importance in removing vibrational energy from $N_2O(00^01)$. Energy transfer to these ring modes is shown to occur through short-range interactions where the energy mismatch is supplied by the translational motion. In all cases, energy transfer probabilities decrease with increasing temperature.

I. Introduction

Gas-phase energy transfer in molecular collisions has been the subject of continuing interest in chemistry and physics for the past several decades.[1−8] In recent years, collisions involving large organic molecules have been studied extensively, revealing valuable information on the rates and the mechanisms of deactivation of the excited molecules through vibration−translation (VT) and/or vibration−vibration (VV) processes. Such collision processes as well as collision-induced intramolecular VV energy transfer are attractive systems for study, since a larger molecule can provide a number of near-resonant energy transfer pathways.[9−18] The importance of such a near-resonant condition has recently been examined by Poel, Alwahabi, and King in their study of energy transfer from $N_2O(00^01$; 2224 $cm^{-1})$ to large organic molecules.[9−11] Since the CD stretching frequencies of many deuterated hydrocarbons are 2224 ± 100 cm^{-1},[19] $N_2O(00^01)$ is a particularly useful reagent in preparing large organic molecules in an excited state.

In this paper, we use the Wentzel−Kramers−Brillouin (WKB) semiclassical procedure to study the vibrational excitation of toluene-d_8 by the collision partner $N_2O(00^01)$. In $N_2O(00^01)-C_6D_5CD_3$, either methyl group CD stretches or benzene ring CD stretches can gain energy from the asymmetric stretch of N_2O. The main purpose of this work is to study energy transfer efficiencies of these stretches and then to establish the principal energy transfer pathways. We also study the temperature dependence of these energy transfer efficiencies in the range 100−500 K.

II. Interaction Model

The nearly exact resonance between $N_2O(00^01)$ and its collision partner occurs when the energy is removed by the methyl group CD mode (ν_a''; 2223 cm^{-1}): $N_2O(00^01) + C_6D_5CD_3(\nu_a''{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_a''{=}1) + \Delta E = +1$ cm^{-1}. Another system that is very close to the resonance condition is $N_2O(00^01) + C_6D_5CD_3(\nu_a'{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_a'{=}1) + \Delta E = +8$ cm^{-1}, where ν_a' represents another methyl CD stretch. The next nearest resonant processes involve energy transfer to the benzene ring CD stretch: $N_2O(00^01) + C_6D_5CD_3(\nu_7{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_7{=}1) + \Delta E = -36$ cm^{-1}, $N_2O(00^01) + C_6D_5CD_3(\nu_{20}{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_{20}{=}1) + \Delta E = -38$ cm^{-1}, $N_2O(00^01) + C_6D_5CD_3(\nu_2{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_2{=}1) + \Delta E = -62$ cm^{-1}.

We present the models of interaction between nitrous oxide and $C_6D_5CD_3$ in Figure 1. The model presented in Figure 1a is appropriate for the interaction of N_2O with the methyl group CD, whereas Figure 1b is for the interaction of N_2O with the benzene ring CD stretch. To simplify the analysis, we make the following assumptions.

(i) A two-dimensional model is used, meaning that the colliding molecules and the center of mass of the system lie on the same plane. To compare the calculated result with the observed data, however, we will employ the modified wavenumber approximation, which will enable us to introduce the impact parameter b by replacing the collision energy E by $E(1 - b^2/b^{*2})$ in the range $0 < b < b^*$, where b^* is chosen such that energy transfer probability is small for $b > b^*$.[20]

(ii) Energy transfer takes place at molecular separations significantly larger than CC, CD, NN, and NO bond distances so that approximate intermolecular atom−atom distances can be determined. These distances will be used to derive the intermolecular potential including both repulsive and attractive terms in exponential forms.

The interaction energies needed to describe the collision of $N_2O(00^01)$ with the ground state $C_6D_5CD_3$ must have terms responsible for the coupling of the asymmetric mode Q_3 of N_2O with the methyl group or benzene ring CD stretch ξ. The interaction coordinates (x, R_1, R_2, R_3) for $N_2O-C_6D_5CD_3$, the bending coordinates (δ_1, δ_2) of N_2O, and the orientation angles (θ, ϕ) are defined in Figure 1. Here x is the distance between the centers of mass of N_2O and $C_6D_5CD_3$. We express the instantaneous NN and NO bond distances $d_{NN} + \Delta d_{NN}$ and $d_{NO} + \Delta d_{NO}$, where Δd_i is the displacement of the bond from its equilibrium distance d_i. These bond displacements are related to the normal coordinates as follows:[21,22]

$$\Delta d_{NN} = l_{11}Q_1 + l_{13}Q_3, \qquad \Delta d_{NO} = l_{21}Q_1 + l_{23}Q_3 \quad (1)$$

where l's are constants dependent on masses and bond distances of N_2O and their explicit forms are given in the Appendix. The angles determining bending displacements are

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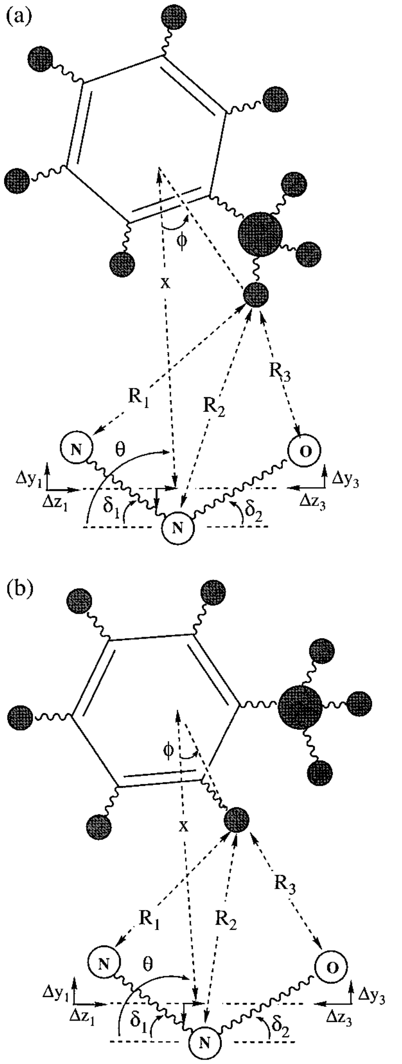

Figure 1. Interaction models for N_2O with (a) the methyl group CD and (b) the benzene ring CD of $C_6D_5CD_3$. The arrows for the displacements for the center N atom of N_2O represent Δy_2 and Δz_2.

$$\delta_1 = \sin^{-1}[(\Delta y_1 + \Delta y_2)/(d_{NN} + \Delta d_{NN})],$$
$$\delta_2 = \sin^{-1}[(\Delta y_2 + \Delta y_3)/(d_{NO} + \Delta d_{NO})]$$

where Δy's are the displacements of N and O from their equilibrium positions depicted in Figure 1. The explicit forms are given in the Appendix.

We will derive the interaction potential energy for $N_2O-C_6D_5CD_3$ here. The atom−atom distances displayed in Figure 1 are typically 4−5 Å, whereas NN and NO bond distances are 1.128 and 1.184 Å, respectively.[23] Therefore, in terms of the normal coordinates of N_2O and the methyl group CD amplitude ($d_{CD} + \xi$), we can derive (neglecting higher-order terms) three atom−atom distances as

$$R_1 = x + [(m_N l_{13} - m_O l_{23})/M]Q_3 - (d_{NN} + l_{13}Q_3)[\cos\theta - (L + K\xi)\sin\theta\sin\phi/R_2] - (L + K\xi)\cos\phi \quad (2a)$$

$$R_2 = x + (m_N l_{13} - m_O l_{23})/M]Q_3 - (L + K\xi)\cos\phi \quad (2b)$$

$$R_3 = x + (m_N l_{13} - m_O l_{23})/M]Q_3 + (d_{NO} + l_{23}Q_3)[\cos\theta - (L + K\xi)\sin\theta\sin\phi/R_2] - (L + K\xi)\cos\phi \quad (2c)$$

where $L = [(d + d_{CC})^2 + d_{CD}^2 - 2(d + d_{CC})d_{CD}\cos\alpha]^{1/2}$, $K = [d_{CD} - (d + d_{CC})\cos\alpha]^{1/2}/L$, $d = 0.940$ Å is the distance between the center of mass of $C_6D_5CD_3$ and the ring carbon to which the methyl group is bonded, $d_{CC} = 1.530$ Å is the equilibrium bond distance between the ring carbon and the methyl group, $d_{CD} = 1.091$ Å is the equilibrium CD bond distance, and $\alpha = 109.5°$ is the tetrahedral angle.

We introduce the above distances in the following interaction potential expressed as a sum of the three Morse-type terms and the dipole−induced dipole energy:

$$U(x,\theta,\phi,Q_1,Q_2,Q_3,\xi) = \sum_{i=1}^{3}[e^{(R_{ie}-R_i)/a_i} - 2e^{(R_{ie}-R_i)/2a_i}] - \frac{\alpha_{C_7D_8}\mu_{N_2O}{}^2(3\cos\theta + 1)}{2(4\pi\epsilon_0)^2x^6} \quad (3)$$

where R_{ie} is the equilibrium value of R_i, $\alpha_{C_7D_8}$ is the polarizability, μ_{N_2O} is the dipole moment, and ϵ_0 is the vacuum permittivity. We consider that the D atom is in interaction with each atom of N_2O in the field created by the two molecules, so we use D and a of the $N_2O-C_6D_5CD_3$ interaction for D_i and a_i in eq 3, where $D = 288$k.[24] We expect the range parameter a to be significantly larger than 0.20−0.25 Å, the values that have often been used for simple collisions.[6] It is physically reasonable to treat a as proportional to the Lennard-Jones range parameter σ. Then using $\sigma(N_2O-C_6D_6) = 4.75$ Å, $\sigma(N_2O-C_6D_5CD_3) = 4.90$ Å,[24] and $a(N_2O-C_6D_6) = 0.33$ Å,[18] we can estimate the range parameter for $N_2O-C_6D_5CD_3$ to be 0.34 Å. When we use the polarizability of 13 Å^3 estimated for toluene[24] and the dipole moment 0.166 D for N_2O,[23] the dipole−induced dipole energy is $-1.8 \times 10^{-20}(3\cos\theta + 1)/x^6$ in joules, where x is in ångstroms. For example, at $x = 5.5$ Å, the orientation average of this long-range interaction energy is -1.6×10^{-24} J. This magnitude is very small compared to $kT = 4.14 \times 10^{-21}$ J at 300 K, but it is comparable to $D = 3.97 \times 10^{-24}$ J. The main effect of this term is to deepen the potential well. This effect can be accounted for by converting the power dependence x^{-6} to an exponential form as $x^{-6} = x_e{}^{-6}(1 - b\ln y)^{-6} = 1 + 6b\ln y + 21b^2\ln^2 y + 56b^3\ln^3 y + ...$, where $y = e^{(x_e-x)/2a}$ and $b = 2a/x_e$. For $2 > y > 0$, $\ln y = (y - 1) - {}^1/_2(y - 1)^2 + {}^1/_3(y - 1)^3 + ...$ Thus, the dipole−induced dipole terms can be written as

$$U_{d-id}(x,\theta) = Wx_e{}^{-6}[3b(7b - 1)e^{(x_e-x)/a} - 6b(7b - 2)e^{(x_e-x)/2a} + (1 - 9b + 21b^2)] \equiv D[\beta_1 e^{(x_e-x)/a} + 2\beta_2 e^{(x_e-x)/2a} + \beta_3] \quad (4)$$

where W is the coefficient of x^{-6} in eq 3. After expanding the exponential parts containing vibrational coordinates, the interaction energy appropriate for treating energy transfer from $N_2O(00^01)$ to the methyl CD stretch can be obtained in the form

$$\begin{aligned}\mathrm{U}(\mathrm{x},\theta,\phi,\mathrm{Q}_3,\xi) = {} & De^{(x_e-x)/a}[\{1 + e^{f_L(\theta,\phi)d_{NN}/a} + e^{-f_L(\theta,\phi)d_{NO}/a}\}e^{L\cos\phi/a} + \beta_1] - 2[\{\mathrm{attr.}\} - \beta_2] + D\beta_3 - \\ & De^{(x_e-x)/a}e^{L\cos\phi/a}[g\cos\phi + \{[g - l_{13}Kf_L(\theta,\phi)]f_{NN}(\theta,\phi) + l_{13}K\sin\theta\sin\phi/R_2\}e^{f_L(\theta,\phi)d_{NN}/a} + \{[g + l_{23}Kf_L(\theta,\phi)]f_{NO}(\theta,\phi) + \\ & l_{23}K\sin\theta\sin\phi/R_{2e}\}e^{-f_L(\theta,\phi)d_{NO}/a}]Q_3\xi/a^2 - 2\{\mathrm{attr.}\} \equiv U_0(x,\theta,\phi) + U'(x,\theta,\phi,Q_3,\xi)\end{aligned} \quad (5)$$

where $g = (m_N l_{13} - m_O l_{23})K/M$, $f_L(\theta,\phi) = (\sin\theta - L\sin\theta\sin\phi/R_{2e})$, $f_{NN}(\theta,\phi) = \cos\phi - d_{NN}\sin\theta\sin\phi/R_{2e}$, and $f_{NO}(\theta,\phi) =$

$\cos\phi + d_{NO}\sin\theta\sin\phi/R_2$. Here {attr.} is the same as the first part including $De^{(x_e-x)/a}$ except that a is replaced by $2a$.

The energy mismatch ΔE is transferred to or from translation. We do not consider the participation of rotational motions of N_2O and $C_6D_5CD_3$ in transferring energy mismatch to be important. In related systems of p-$C_6H_4F_2$ with H_2, D_2, and N_2, where the organic molecule is in an excited state, Mudjijono and Lawrance have shown that there is no evidence of vibration−rotation (VR) energy transfer.[14] It is also of interest to note that the contribution of VR energy transfer is not significant in the de-excitation of highly excited O_2 by N_2O and CO_2.[25] However, in the collision involving large molecules, the direction of approach significantly modifies interaction energies, thus influencing energy transfer processes. A reasonable approach to account for this aspect is averaging eq 5a over θ and ϕ. While N_2O can be oriented at all different directions between 0 and 2π, only the methyl side of the target is responsible for energy transfer (see Figure 1a). Thus, we average the interaction energies over $\phi = 0$ to $\pi/3$ (i.e., $\pi/6$ both sides of the methyl group). This picture changes when we consider energy flow between N_2O to the ring CD stretching vibration, in which case any one of five ring CD stretches can remove energy from N_2O. Therefore, a physically reasonable approach is to average over $^5/_6$th the ring, leaving the methyl group region out. We write the orientation average of eq 5 in two parts as

$$\bar{U}_0(x) = D[Ae^{(x_e-x)/a} - 2Be^{(x_e-x)/2a} + \beta_3]$$

$$\text{and}\qquad \bar{U}'(x,Q_3,\xi) = D[A'e^{(x_e-x)/a} - 2B'e^{(x_e-x)/2a}]Q_3\xi$$

where A, B, A', and B' are the θ,ϕ-average of the corresponding terms in eq 5. A more rigorous approach to the interaction model is to use a full dimensional potential energy surface based on ab initio calculations. However, such calculations do not appear possible at present for collisions involving large molecules. Until such a PES becomes available, the present procedure of formulating the exponential interactions in terms of atom−atom and long-range attractions is of practical value in handling collisions involving large molecules.

III. Energy Transfer to Methyl Group CD Stretch Modes

For the near-resonant energy transfer from $N_2O(00^01)$ to the methyl group CD stretch, we use the WKB wave functions[26]

$$\psi_i(E,x) = c_i\{2m[E - \bar{U}_0(x)]\}^{-1/4} \cos\left\{\frac{(2m)^{1/2}}{\hbar}\int_{x_{o,i}}^{x}[E - \bar{U}_0(x)]^{1/2}dx\right\}, \qquad x > x_{o,i} \quad (6a)$$

$$\psi_f(E+\Delta E,x) = c_f\{2m[(E+\Delta E) - \bar{U}_0(x)]\}^{-1/4}\cos \left\{\frac{(2m)^{1/2}}{\hbar}\int_{x_{o,f}}^{x}[(E+\Delta E) - \bar{U}_0(x)]^{1/2}\,dx\right\}, \qquad x > x_{o,f} \quad (6b)$$

in the distorted wave approximation,[27,28] where the pertinent step is the evaluation of the perturbation integral $\int\psi_i(E,x)[A'e^{(x_e-x)/a} - B'e^{(x_e-x)/2a}]\psi_f(E+\Delta E,x)\,dx$. Here $c_i = (2\pi mE)^{1/4}$, $c_f = [2\pi m(E+\Delta E)]^{1/4}$, where m is the reduced mass of the collision system and x_o is the turning point. Since eqs 6a and 6b describe the waves on the right-hand side of the turning point, they are appropriate for treating vibrational energy transfer processes taking place at long range. The evaluation of the perturbation integral yields the energy transfer probability expression

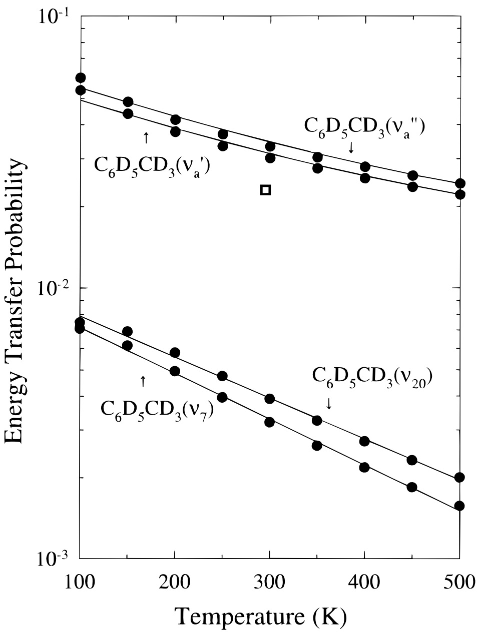

Figure 2. Temperature dependence of energy transfer probabilities. The top two curves are for $N_2O(00^01) + C_6D_5CD_3(\nu_a''=0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_a''=1) + \Delta E = +1\ cm^{-1}$ and $N_2O(00^01) + C_6D_5CD_3(\nu_a'=0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_a'=1) + \Delta E = +8\ cm^{-1}$ based eq 7. The lower two curves are for $N_2O(00^01) + C_6D_5CD_3(\nu_7=0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_7=1) + \Delta E = -36\ cm^{-1}$ and $N_2O(00^01) + C_6D_5CD_3(\nu_{20}=0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_{20}=1) + \Delta E = -38\ cm^{-1}$ based on the short-range interaction model of ref 18. The experimental point (□) is taken from ref 10.

$$P(E) = 32\pi\mu D(a/\hbar)^2|\langle 00^01,0|Q_3\xi|00^00,1\rangle|^2| \int_0^{y^*}\frac{(A'y - 2B')}{(Y_jY_f)^{1/2}}\cos\left\{\rho Y + \frac{\rho B}{A^{1/2}}\sin^{-1}\left[\frac{Ay - B}{(B^2 + AE/D)}\right] - \rho\left(\frac{E}{D}\right)^{1/2}\ln\left[\frac{Y + (E/D)^{1/2}}{y} + B\left(\frac{D}{E}\right)^{1/2}\right] + \frac{\rho}{2}\left(\frac{E}{D}\right)^{1/2}\ln\left(A + \frac{B^2D}{E}\right) - \frac{\rho\pi B}{2A^{1/2}}\right\}\cos\{...\}\,dy|^2 \quad (7)$$

where $Y = (-Ay^2 + 2By + E/D)^{1/2}$, $y = e^{(x_e-x)/2a}$, and $\langle 00^01,0|Q_3\xi|00^00,1\rangle$ is the vibrational matrix element. In eq 7, cos{...} is the same as the first cosine factor except that E is replaced by $E+\Delta E$ throughout. Here the value of x^*, determined numerically, is the distance where energy transfer is most likely to occur. To study the temperature dependence of energy transfer processes, we average eq 7 over the Boltzmann distribution of collision energies and integrate over the impact parameter b after replacing E by $E(1 - b^2/b^{*2})$ in the range of $0 < b < b^*$. With this modification, we now have the probability as a function of both E and b, $P(E,b)$ and the E,b integration gives $P(T)$. For endoergic energy transfer from translation to vibration, the lower limit of the Boltzmann integration is $|\Delta E|$. For the energy transfer from $N_2O(00^01)$ to $C_6D_5CD_3(\nu_a'')$, the energy mismatch is only $+1\ cm^{-1}$ and $\Delta\nu = 2$, the smallest number possible for VV energy transfer. At 295 °C the calculated probability is 0.033, representing a fairly efficient energy transfer process. This value compares well with the observed probability of 0.023.[10] The temperature dependence of calculated probabilities over the temperature range 100−500 K is shown in Figure 2. The probability is as high as 0.059 at 100 K, but it decreases to 0.024 at 500 K, a negative temperature dependence that is characteristic of near-resonant VV energy transfer processes.[6] However, over this temperature range, the change of probability is not very large. Even at a temperature as high as 1000 K, the probability is found to be 0.016. We note the upper limit of the y (or x) integration range in eq 7 corresponds to $x^* = x_e + 2a \ln y^*$, where y^* is determined numerically to be 0.559. Since $\sigma = 4.90$ Å for $N_2O-C_6D_5CD_3$, we can estimate the equilibrium distance $x_e = 2^{1/6}\sigma = 5.50$ Å. Hence, this upper limit corresponds to 5.90 Å, which clearly indicates the transfer of vibrational energy from $N_2O(00^01)$ to $C_6D_5CD_3$ taking place at long range where the attractive interaction is of primary importance. Thus, for resonant or near-resonant energy transfer, such long-range interactions result in negative dependence of energy transfer probability on temperature. The ν_a'' curve shown in Figure 2 can be closely fit to the linear equation $\log P(T) = -(1.17-9.32) \times 10^{-4}T$. Another near-resonant case is the energy transfer to the ν_a' mode of the methyl group CD stretch: $N_2O(00^01) + C_6D_5CD_3(\nu_a'{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_a'{=}1) + \Delta E = +8\ \mathrm{cm}^{-1}$. The result for this process is only slightly different from the ν_a'' case (see Figure 2). The energy transfer probability is 0.030 at 295 K.

For the transfer of the N_2O asymmetric vibrational energy to the ν_7 mode of the CD stretch on the benzene ring, $N_2O(00^01) + C_6D_5CD_3(\nu_7{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_7{=}1)$, the energy mismatch is $-36\ \mathrm{cm}^{-1}$ but $\Delta\nu$ is still 2. Another process closely related to this is the ν_{20} mode excitation: $N_2O(00^01) + C_6D_5CD_3(\nu_{20}{=}0) \rightarrow N_2O(00^00) + C_6D_5CD_3(\nu_{20}{=}1) + \Delta E = -38\ \mathrm{cm}^{-1}$. However, both ν_7 and ν_{20} are CD stretch modes on the benzene ring, and to describe their excitation processes, it is necessary to use the atom−atom distances defined in Figure 1b. The explicit forms of these distances used to derive $U(x,\theta,\phi,Q_3,\xi)$ are given in the Appendix. The calculated VV probabilities based on the model of long-range interactions for these two processes at 295 K are 3.99×10^{-4} and 3.02×10^{-4}, respectively. These values are 2 orders of magnitude smaller than that of the ν_a'' or ν_a' excitation case. It is now important to recognize that in these ring-mode excitations the magnitude of energy mismatch is significant so the use of the model that emphasizes long-range interactions alone may not be suitable. As the colliding molecules approach each other, the VV process of $N_2O(00^01)$ to $C_6D_5CD_3(\nu_7 \text{ or } \nu_{20} = 0)$ takes place efficiently near 5.90 Å and then the translational motion follows to supply $|\Delta E|$ (i.e., a VT process) so that toluene can reach the excited state $C_6D_5CD_3(\nu_7 \text{ or } \nu_{20} = 1)$. Although the magnitude of $|\Delta E|$ is not particularly large, the inefficiency of the latter process is serious enough to bring down the probability of the overall excitation process by a large extent. Thus, this VT process is a bottleneck step. We now look into this aspect in the following section.

IV. Short-Range Interaction Model

When ΔE is large, the colliding molecules must approach within close range of each other, where repulsive interactions are of major importance, for VT energy transfer to take place. We expect this range to lie well inside the distance 5.90 Å of the long-range model. Therefore, the contribution coming from the wave functions that have penetrated into the left-hand side of the turning point will have to be considered in formulating the transition probability. On this side the wave functions decrease exponentially while the interaction potential increases. Such short-range interaction is inherent in describing the transfer of vibrational energy to translation. Thus, the integrand of the perturbation integral $\int\psi_i(E,x)[A'e^{(x_e-x)/a} - B'e^{(x_e-x)/2a}]\psi_f(E+\Delta E,x)\,dx$ takes a maximum value at x^*. Recognizing this situation for the exponentially varying wave functions, we have already derived a probability expression appropriate for the present process in ref 18. The values of ν_7 and ν_{20} excitation probabilities obtained by use of this probability expression at 295 K are 0.0033 and 0.0039, respectively, which are 1 order of magnitude larger than those obtained above for the long-range model. For the ν_7, ν_{20}, and ν_2 excitation processes, corresponding to $\Delta E = -36$, -38, and $-62\ \mathrm{cm}^{-1}$, respectively, the most probable distances x^* at which the transfer of energy mismatch occurs are 5.27, 5.24, and 4.99 Å. Since the potential minimum distance of the N_2O−toluene interaction is 5.50 Å, these distances lie just inside the repulsive region and they are significantly shorter than 5.90 Å of the long-range model. For these excitation processes where $|\Delta E|$ falls in the range of 30−60 cm^{-1}, it is likely that both long-range and short-range interactions participate in energy transfer even though the former interaction is of minor importance. Then it is reasonable to express the probability as a sum of short-range and long-range contributions. For the ν_7 and ν_{20} excitation processes, the probabilities obtained summing the long-range and short-range contributions are 0.0036 and 0.0043 at 295 K. Therefore, the values plotted for these two processes in Figure 2 will rise slightly, but the slope remains the same.

According to the short-range interaction model, the ν_7 excitation probability decreases from 0.0071 at 100 K to 0.0016 at 500 K. The corresponding values for the ν_{20} excitation are 0.0075 and 0.0020 (see Figure 2). The temperature dependence of the energy transfer probability for both cases is linear. For example, for the ν_7 excitation the semilogarithmic plot closely obeys $\log P(T) = A + BT$, where $A = -1.97$ and $B = -1.69 \times 10^{-3}\ \mathrm{K}^{-1}$. In comparing the ν_7 and ν_{20} probabilities, we note that the values for the ν_{20} excitation are slightly larger despite a larger amount of translational energy being involved. This situation results because the most probable distance x^* at which the VT transfer takes place is shorter in the ν_{20} excitation case. Hence the potential energy at this distance $U(x^*)$ is slightly larger for the ν_{20} case. That is, $U(x^*) = 6.02 \times 10^{-21}$ J for the ν_{20} case compared with 5.40×10^{-21} J for ν_7. This leads to a wider range for the E integration in the former case, thus yielding a larger probability. Such a trend persists as long as $|\Delta E|$ is less than 60 cm^{-1}. When $|\Delta E|$ exceeds this range, however, the difficulty of transferring a large amount of the translational energy to or from vibration dominates the effect of the E-integration range, thus leading to a smaller VT probability.

The temperature dependence of the short-range model reveals another important aspect of the $N_2O-C_6D_5CD_3$ collision. The rate of change of the negative temperature dependence of $P(T)$ slows down as the magnitude of energy mismatch increases, eventually becoming positive for $|\Delta E| > 60\ \mathrm{cm}^{-1}$. For example, for $\Delta E = -80\ \mathrm{cm}^{-1}$ the energy transfer probability rises from 0.0014 to 0.0070 when the temperature increases from 100 to 300 K. At 500 K, the probability is as large as 0.010. If we take the magnitude of energy mismatch as large as $-300\ \mathrm{cm}^{-1}$, where the translational motion must now transfer a large amount of energy, $P(T)$ is as low as 6.39×10^{-8}, 7.82×10^{-6}, 2.93×10^{-5} at 100, 300, and 500 K, respectively. Here we have set $\Delta\nu = 2$. For a larger quantum number change, we would obtain still lower probabilities. It is interesting to note a semilogarithmic plot of these probabilities of the short-range model against $T^{-1/3}$ gives a straight line, as shown in Figure 3. This $\log P(T)$ −

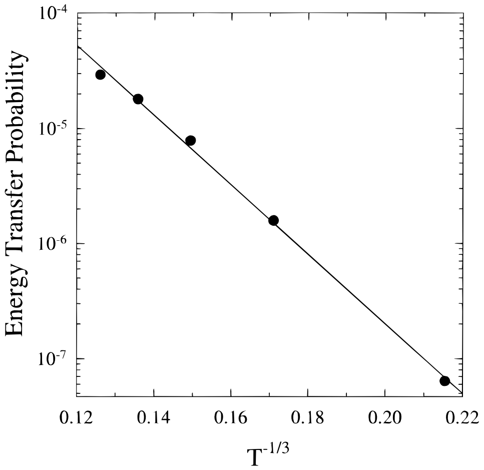

Figure 3. Temperature dependence of energy transfer probabilities obtained using the model of short-range interactions with $\Delta E = -300$ cm^{-1}.

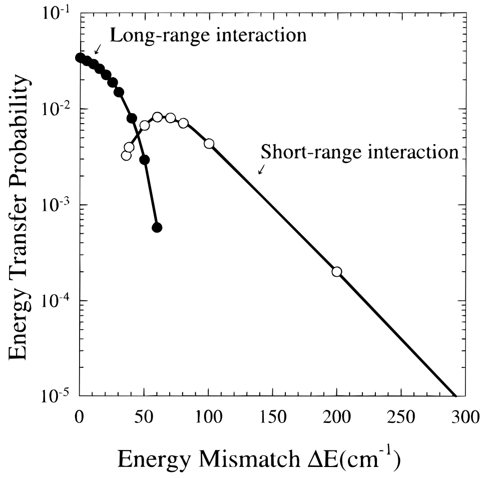

Figure 4. Variation of energy transfer probabilities with energy mismatch at 300 K. Results of both the long-range interaction model for the methyl CD stretches and the short-range model for the benzene ring CD stretches are shown.

$T^{-1/3}$ relation is not obvious in the form of the short-range probability expression given in ref 18, but numerical integration over the collision energy and impact parameter gives this linear dependence, the well-known Landau−Teller plot of VT energy transfer.[6,29] The sharp increase of P(T) with rising temperature seen in Figure 3 reflects an increased role of short-range interactions in transferring a large amount of energy by the translational motion. Such positive temperature dependence is indicative of the energy mismatch being transferred to or from translation on the left-hand side of the turning point, where energetic collisions have taken place.

Finally, we compare the results of the long-range interaction model (i.e., eq 7) for the methyl group CD stretch and the short-range model[18] for the benzene ring CD stretch. In comparing these two models, we remember that the entire amount of the $N_2O(00^01)$ vibrational energy is transferred to toluene through a VV process when the colliding molecules are at long range. Besides the obvious difference in the interaction model represented by Figure 1a,b, however, the short-range model then considers the molecules approaching close range for the transport of ΔE. The results of these two models are plotted in Figure 4 as a function of energy mismatch. The curve starting out from the ν_a'' value 0.033 and then moving rapidly downward to 5.74×10^{-4} at 60 cm^{-1} is the result of the long-range model. Note that $P(T) = 0.034$ for $\Delta E = 0$. Real and hypothetical VV channels for the excitation of methyl group CD stretch modes with $\Delta\nu = 2$ and $|\Delta E|$ supplied by the translational motion at long range give $P(T)$ that falls on this curve. Equation 7 indicates that the probability oscillates as energy mismatch continues to increase. The first minimum of such oscillation occurs near 65 cm^{-1}, but as discussed above this equation becomes less reliable for the collision with such a large energy mismatch. We consider long-range interactions to play a major role in the collisions in which the energy mismatch is sufficiently small (± 20 cm^{-1}). Beyond this range they predict energy transfer probabilities that are too small. On the other hand, as $|\Delta E|$ increases, more energy will have to be transferred by translation, so the role played by short-range interactions becomes increasingly important. The curve in Figure 4 covering $|\Delta E|$ from 30 to 300 cm^{-1} represents this case for the benzene ring CD modes with $\Delta\nu = 2$; VV channels with the VT step transferring ΔE at short range follow this curve. Thus, in $N_2O{-}C_6D_5CD_3$, all those channels involving the ring-mode CD stretches play a minor role in removing the vibrational energy of $N_2O(00^01)$. We note the linear temperature dependence of $\log P(T) - T^{-1/3}$ seen above 100 cm^{-1} is a characteristic of VT energy transfer and shows the probability falling off by roughly a factor 10 for each 100 cm^{-1} of energy mismatch. The shapes of these two curves resemble those of earlier studies summarized in Yardley's book.[6]

V. Concluding Comments

The WKB calculation of energy transfer probabilities for the $N_2O(00^01)$-$C_6D_5CD_3$ collision shows the principal energy transfer pathways are the excitation of the ν_a'' and ν_a' CD stretch modes of the methyl group. These energy transfer processes with small ΔE and quantum number change of 2 are dominated by long-range interactions. In the excitation of the ν_7 and ν_{20} CD modes on the benzene ring, the VT step taking place at short range plays an important role in transferring ΔE. Thus, the transfer of vibrational energy to these two benzene-ring modes is much less efficient. In the temperature range 100−500 K, the logarithm of energy transfer probabilities for all these processes decreases nearly linearly with increasing temperature.

Appendix

The coefficients of normal coordinates given by eq 1 for N_2O are

$$l_{11} = \left[cd_{NN} - s\left(\frac{m_O}{m_N^{\,2}M}\right)^{1/2}(m_N d_{NN} + 2m_N d_{NO})\right] I^{-1/2} \quad \text{(A1)}$$

$$l_{13} = \left[sd_{NN} + c\left(\frac{m_O}{m_N^{\,2}M}\right)^{1/2}(m_N d_{NN} + 2m_N d_{NO})\right] I^{-1/2} \quad \text{(A2)}$$

$$l_{21} = \left[cd_{NO} + \frac{s}{(m_N M)^{1/2}}(m_O d_{NO} + m_{NO} d_{NN})\right] I^{-1/2} \quad \text{(A3)}$$

$$l_{23} = \left[sd_{NO} - \frac{c}{(m_N M)^{1/2}}(m_O d_{NO} + m_{NO} d_{NN})\right] I^{-1/2} \quad \text{(A4)}$$

where $c = 0.9734$, $s = 0.2284$, $M = 2m_N + m_O$, $m_{NO} = m_N + m_O$, and I is the moment of inertia. The displacements of N and O atoms from their equilibrium positions indicated in Figure 1 are

$$\Delta y_1 = -(m_O/MI)^{1/2} d_{NO} Q_2, \quad \Delta y_2 = (m_O/MI)^{1/2}(d_{NN} + d_{NO})Q_2, \quad \Delta y_3 = -(m_N{}^2/m_O MI)^{1/2} d_{NN} Q_2 \tag{A5}$$

$$\Delta z_1 = -\{[(m_N + m_O)l_{11} + m_O l_{21}]Q_1 + [m_N + m_O)l_{13} + m_O l_{23}]Q_3\}/M \tag{A6}$$

$$\Delta z_2 = [(m_N l_{11} - m_O l_{21})Q_1 + (m_N l_{13} - m_O l_{23})Q_3]/M \tag{A7}$$

$$\Delta z_3 = [(m_N l_{11} + 2m_N l_{21})Q_1 + (m_N l_{13} + 2m_N l_{23})Q_3]/M \tag{A8}$$

The atom−atom distances for N_2O to the benzene ring D atom indicated in Figure 1b are

$$R_1{}' = x + [(m_N l_{13} - m_O l_{23})/M]Q_3 - (d_{NN} + l_{13}Q_3)[\cos\theta - (L' + K'q)\sin\theta\sin\phi/R_2] - (L' + K'q)\cos\phi \tag{A9}$$

$$R_2{}' = x + (m_N l_{13} - m_O l_{23})/M]Q_3 - (L' + K'q)\cos\phi \tag{A10}$$

$$R_3{}' = x + (m_N l_{13} - m_O l_{23})/M]Q_3 + (d_{NO} + l_{13}Q_3)[\cos\theta - (L' + K'q)\sin\theta\sin\phi/R_2] - (L' + K'q)\cos\phi \tag{A11}$$

where $L' = [d'^2 + (d_{CC}' + d_{CD})^2 - 2d'(d_{CC}' + d_{CD}')\cos 60°]^{1/2}$ and $K' = [d_{CC}' + d_{CD} - d\cos\alpha]^{1/2}/L'$. Here d' is the distance between the benzene ring center and the center of mass 0.455 Å, d_{CC}' is the ring CC bond distance 1.395 Å, and d_{CD}' is the ring CD bond distance 1.084 Å.[23]

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