Electronically nonadiabatic mechanism of the vibrational relaxation of NO in Ar: Rate coefficients from ab initio potentials and asymptotic coupling

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In this paper, the electronically nonadiabatic Landau-Zener (LZ) mechanism for the vibrational relaxation of NO = 1 → NO = 0 of NO(X^2Π) in collisions with Ar(1S_0) is discussed. It corresponds to nonadiabatic transitions between two crossing vibronic potential energy surfaces (PESs) originating from vibrational states of the collision complex and supported by two coupled electronic PESs. The LZ rate coefficients LZk_{10} are calculated within the uniform Airy approach in the reaction coordinate approximation with parameters derived from ab initio PESs and an asymptotic estimation of the Franck-Condon factor in the nonadiabatic coupling region. The rate coefficients are close to the experimental rate coefficients available over the range of 900–2500 K, where the electronically adiabatic Landau-Teller (LT) mechanism with the rate coefficients LTk_{10} does not make a noticeable contribution to the total relaxation rate. The ratio LZk_{10}/LTk_{10} increases with temperature and the LZ and LT mechanisms have comparable rates at about 4000 K. Published by AIP Publishing. https://doi.org/10.1063/1.5038619

I. INTRODUCTION

The vibrational relaxation of NO in Ar represents a paradigm for vibrational to translational/rotational energy transfer in collisions of a diatom in an open electronic state with chemically inert atoms. Experimental studies in shock waves at high temperatures1,2 indicated deviations in the measured rate coefficients from Landau–Teller (LT)3,4 behavior, such as those formulated by the Schwartz–Slawsky–Herzfeld (SSH) theory5,6 and documented in Refs. 7 and 8. This discrepancy was attributed to a curve-crossing mechanism of the Landau–Zener (LZ) type9,10 which is related to nonadiabatic transitions between two crossing vibronic (vibrational–electronic) potential energy surfaces (PESs) in contrast to the nonadiabatic vibrational transitions between the vibrational states within a single adiabatically isolated electronic state such as that assumed for the LT mechanism. Earlier attempts to estimate the relaxation rate coefficient11,12 were based on the Wentzel-Kramers-Brillouin (WKB) Landau expression13 for the transition probability but were hampered by the absence of reliable vibronic PESs, in particular the energy of the crossing point which is expected to dominate the temperature dependence of the rate coefficients. Recent calculations of the adiabatic electronic PESs for the NO–Ar system14–16 now permit to determine the crossing energy and thus open the possibility for a determination of the rate coefficients. Our recent work17,18 was aimed at the estimation of tunneling corrections to high-temperature rate coefficients, the latter being identified with experimental values at 1500 K.19,20 In the present work, we calculate the rate coefficients in the uniform Airy (UAi) approximation21 generalizing the original Landau result13 for collision energies close to and below the crossing energy of the potentials. Accordingly, the plan of this article is as follows. Section II describes the Born-Oppenheimer (BO) electronic PESs for the NO–Ar system on the basis of the recent ab initio result, and Sec. III discusses the nonadiabatic coupling between the vibronic PESs. Section IV presents the derivation in the LZ rate coefficients in the reaction-coordinate (RC) approximation within its surface-hopping version. Quantum corrections to the calculated LZ rate coefficients in the uniform Airy approximation are described in Sec. V. In Sec. VI, the calculated curve-crossing rate coefficients are compared with the experimental results and the interplay between the curve-crossing LZ and the non-crossing LT pathways of relaxation is discussed. Section VII concludes the article. Details of the calculation of coupling coefficients in the asymptotic approach for the exchange interaction are presented in the Appendix.

II. BO ELECTRONIC AND VIBRONIC PESs OF THE Ar(1S) + NO(2Π) SYSTEM

For an Ad + BC(2Π) system, there are two doubly degenerate BO states (Kramers degeneracy) and two BO PESs that depend on three coordinates: the internuclear distance r in the diatom BC, the interfragment separation R, and the angle θ between the molecular and the collision axes. In the asymptotic region, R → ∞, these states are specified by the absolute value \( \Omega \) of the projection of the total (orbital + spin) electronic angular momentum onto the molecular axis of BC, with \( \Omega = 1/2 \) and 3/2, and split by the spin–orbit coupling constant \( A \). In the region of strong electrostatic and exchange

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interactions, when the energy difference between the two BO PESs is much larger than the spin–orbit coupling, the BO states can be specified by the projections of the electron spin onto a space-fixed axis and the symmetry character (symmetric or antisymmetric) of the coordinate electronic wave function \((A', A''\) states that correspond to the \(2A', 2A''\) spin-coordinate states) with respect to the reflection in the system plane (i.e., in the ABC plane). The BO energies of these states, \(U_A(r, R, 0)\) and \(U_{A'}(r, R, 0)\), are then calculated neglecting the spin–orbit interaction (within accuracy \(A^2/|U_A - U_{A'}|\)).

The solution of the wave equation for vibrational motion of NO in the field of the potentials \(U_A(r, R, 0)\) and \(U_{A'}(r, R, 0)\) yields the adiabatic vibronic (vibrational + electronic) VE wave functions \(|A', v'\rangle = |A')(v'; A'\rangle\) and \(|A'', v''\rangle = |A'')(v''; A''\rangle\), with the vibrational functions \(|v'; A'\rangle\), \(|v''; A''\rangle\) supported by different electronic PESs. The VE functions \(|A', v'\rangle\) and \(|A'', v''\rangle\) correspond to the VE eigenvalues \(V_{A', v'}(R, 0)\) and \(V_{A'', v''}(R, 0)\).

The rate-determining step in the vibrational relaxation of NO, \(v = 1 \rightarrow v = 0\), is assumed to be the nonadiabatic transition \(|i\rangle \equiv |A'', v''\rangle = 1 \rightarrow |f\rangle \equiv |A', v'\rangle = 0\) in the region of the resonance, where the vibronic potentials \(V_i(R, 0) \equiv V_{A', v'}(R, 0)\) and \(V_f(R, 0) \equiv V_{A'', v''}(R, 0)\) cross such that

\[
V_i(R, 0) = V_f(R, 0). \tag{2.1}
\]

A solution of Eq. (2.1) for \(R\) determines the crossing line (CL), \(R = R_c(0)\), which plays the part of the dividing surface (DS) in a transition state theory approach (see Sec. III).

Adiabatic vibronic PESs for the states \(|A'', v''\rangle\), \(|A', v'\rangle\) are recovered from the adiabatic electronic PESs for the states \(|A'\rangle\), \(|A\rangle\) calculated at the equilibrium internuclear distance in NO, at \(r = r_c\), by a perturbation technique valid for low vibrational states. We estimate that the adiabatic correction to the perturbed vibrational states is small, such that an approximation of \(V_{A', 0}(R, 0)\) and \(V_{A', 1}(R, 0)\) by the superposition of the potentials \(V'(R, 0) = U_A(r_c, R, 0)\) and \(V''(R, 0) = U_A(r_c, R, 0)\) and the vibrational energies of the free NO molecule, \(E_v\), appears acceptable. If the energy is counted from the first vibrational level of the free NO molecule, then the vibronic PESs \(V_i(R, 0)\) and \(V_f(R, 0)\) can be identified with the electronic PES \(V''\) and the shifted electronic PES \(V'\), respectively,

\[
V_i(R, 0) = V''(R, 0), \tag{2.2}
\]

\[
V_f(R, 0) = V'(R, 0) - \Delta E_{10},
\]

where \(\Delta E_{10}\) denotes the energy difference between the first and the ground vibrational levels of the free NO molecule, \(\Delta E_{10} = E_1 - E_0 = 1876 \text{ cm}^{-1}\). We note in passing that a small adiabatic correction to the perturbed vibrational states, which is neglected in Eq. (2.2), is of crucial importance in the calculation of the coupling matrix elements (see Sec. III). In what follows, we adhere to this approximation in Eq. (2.2) and we use the \textit{ab initio} potentials \(V'(R, 0)\) and \(V''(R, 0)\) such as those presented in Refs. 14–16 and recalculated here by numerical codes put at our disposal by Alexander.

The basic features of the potentials \(V'(R, 0)\) and \(V''(R, 0)\) and their difference \(\Delta V(R, 0) = V'(R, 0) - V''(R, 0)\) are better understood by considering in more detail the electronic structure of the NO–Ar system. The electronic states \(A'\) and \(A''\) of the NO–Ar system arise from the electronic states \(X^2\Pi', (1\sigma^2)(1\pi^2)(5\sigma^2)(2\pi')\) and \(X^2\Pi'', (1\sigma^2)(1\pi^2)(5\sigma^2)(2\pi'')\) of NO. Since the system plane is the nodal plane for the \(2\pi''\) orbital, the potential in the repulsive region of \(R, 0\) for the \(2\pi'\) state, \(V''(R, 0)\), is dominated by the exchange interaction of the electrons of the Ar atom with the core electrons of NO in the \((1\pi^2)(1\sigma^2)(5\sigma^2)^2(2\pi'')\) configuration, while for the \(2\pi'\) state, \(V'(R, 0)\), besides this interaction also includes the exchange interaction between the electrons of the noble gas atom and the electron of NO occupying the \(2\pi'\) orbital. The difference in the potentials \(\Delta V = V'' - V'\) is determined mainly by the exchange interaction of electrons of the noble gas atom with the electron of NO on the \(2\pi'\) orbital. According to the asymptotic theory of the exchange interaction, \(24\) \(\Delta V\) is proportional to the overlap of the \(2\pi'\) orbital of NO with the outer orbital of Ar at the center of the NO–Ar collision complex location. This is illustrated in Fig. 1 by a set of equipotential lines (ELs) in the repulsive region of the contour map of the \(V_A(R, 0)\) (red lines) and \(V_B(R, \theta)\) (blue and green lines) with the osculating points for CL and EL. The dashed straight lines indicate the boundaries of the angular sector discussed in Figs. 2 and 3, which is important in the calculation of the rate coefficient.

The \(V''(R, 0)\) PES, for which the exchange interaction with the electron occupying the \(2\pi''\) molecular orbital (MO) is absent, has a simple structure and is similar to that for an \(N_2–Ar\) system. The qualitative features of the CL with its two lobes originate from the two-lobe structure of the \(2\pi'\) MO which is qualitatively similar to the two-lobe structure of the \(dx^2\) atomic orbital (AO) centered on the molecular axis between the N and O atoms. The position of the Coulomb center of this orbital is shifted by \(\Delta r_c\), with respect to the center of mass of NO toward the N atom of the NO molecule, as suggested by the form of the SCF LCAO-MO \(2\pi'\) in which the weight of the \(p(n)\) AO is larger than that of \(p(o)\).\(^\text{23}\) Respectively, the radial factor of the \(dx^2\) AO will be modified by an angular factor, which will affect the overall angular dependence of the shifted \(dx^2\) AO. As a result, the lobe of

![FIG. 1. Contour map of the NO–Ar PES \(V''(R, 0)\) (full and dotted red lines) and two lobes of the crossing line \(R = R_c(0)\) (full blue line in the first quadrant and full green line in the second quadrant). The dotted lines touch the blue and green lines at the osculating points (marked by small circles) where the energies of the \(V''(R, 0)\) PES along the dotted lines attain local minima (see the text for more details).](image-url)
The quantities that enter into the expression for the rate coefficient (see Sec. III) are the crossing distance $R_c(\theta)$, the parameter $\alpha_c(\theta)$ that characterizes the rate of divergence of the vibronic PESs near the CL, and the energy $E_c(\theta)$ of the initial vibronic PES and its quadratic (q) approximation $E_c^q(\theta)$ along the CL. The quantities $\alpha_c(\theta)$ and $E_c^q(\theta)$ are defined as

$$\alpha_c(\theta) = \left| \frac{\partial \Delta V(R, \theta)}{\partial E_{10}} \right|_{R=R_c(\theta)} = \frac{\Delta E_{10}}{\alpha_c(\theta)}$$

and

$$E_c^q(\theta) = E_c + \frac{\alpha_c(\theta)}{2} (\theta - \theta_0)^2$$

with $E_c(\theta) = \partial^2 E_c(\theta)/\partial \theta^2 \bigg|_{\theta=\theta_0}$. Plots of $R_c(\theta)$, with the “divergence boundaries” $R_c^\pm(\theta) = R_c(\theta) \pm 1/2\alpha_c(\theta)$, are shown in Fig. 2, while plots of $E_c(\theta)$ and $E_c^q(\theta)$ are shown in Fig. 3. A weak dependence of $\alpha_c(\theta)$ on $\theta$ (illustrated by three values of $\alpha_c(\theta)$ across the angular range $0.2\pi - 0.4\pi$) and its absolute value are in line with predictions from the asymptotic theory of the exchange interaction. Numerical values of parameters that characterize the optimal configuration are summarized in Table I.

### III. COUPLING BETWEEN INITIAL AND FINAL BO VIBRONIC STATES

The coupling between the initial and the final vibronic states (defined within the BO electronic approximation with the spin–orbit interaction neglected) is due to the rotation of the system plane and the spin–orbit interaction.\(^\text{10}\) The respective coupling operator within the classical description of overall rotation is written in the form

$$\hat{W} = \omega_\alpha \hat{L}_n + A \hat{L}_n \hat{S}_n,$$  

where $\omega_\alpha$ is the projection of the angular velocity of rotation of the system plane onto the molecular axis $\mathbf{n}$; $\hat{L}_n$ and $\hat{S}_n$ are the operators of the projections of the electronic angular momentum and electronic spin onto $\mathbf{n}$, respectively; and $A$ is the spin–orbit coupling coefficient. The expression in Eq. (3.1) is written under the assumption that the main contribution to the electronic states $A'$ and $A''$ of the $AB + X$ system comes from the system functions built mainly from the MO functions with the quantization axis directed along $\mathbf{n}$. In addition, the Coriolis interaction between spin and system rotation is neglected.

If the coupling given by Eq. (3.1) is neglected, the dynamics of the $AB + X$ system corresponds to the rotationally inelastic scattering on a set of vibronic PESs of $A'$ and $A''$ symmetry. For sufficiently large $R$, the angular dynamics of the $AB$ pair on each PES corresponds to a perturbed linear rotor (LR) motion with the quantization axis for the angular momentum.
of the rotor directed along $\mathbf{R}$. If the first term in Eq. (3.1) is taken into account and is diagonalized on the basis of LR states, the latter become symmetric top (ST) states. They correspond to the $|j, m, \Lambda\rangle$ rotational states of a free AB molecule in the electronic PI state with $\Lambda = \pm 1$ and $j \geq 1$ in Hund’s case $b$ nomenclature. If the second term in Eq. (3.1) is now taken into account, the $|j, m, \Lambda\rangle$ states transform into $|j, m, \Omega\rangle$ states of the electronic $2\Sigma$ state with $\Omega = \pm 1/2, \pm 3/2$ and $j \geq |\Omega|$ in Hund’s case $a$ nomenclature. If, finally, the terms in Eq. (3.1) are supplemented by the Coriolis interaction of the spin with the molecular rotation, the rotational states $|j, m, \Omega\rangle$ become coupled, giving rise to the states $|j, m, F\rangle$ with $F = F_1, F_2$ of the intermediate $a-b$ Hund case. The rather complicated dynamics of the collision complex in the asymptotic region (i.e., for large $R$) does not show up in the $|A'', \nu'' = 1\rangle \rightarrow |A', \nu' = 0\rangle$ vibrational relaxation rate coefficients since the nonadiabatic mixture between the asymmetric states by the relative motion $v$ is then represented by the matrix element of the electronic part of the matrix element, $v^2$, between the VE states $|\bar{\nu}\rangle \rightarrow |\bar{\nu}'\rangle$, where $\bar{\nu}$ is then identified with $\nu - \nu' = 0$, i.e.,

$$\begin{align*}
W_{i,f} &= S^\text{vib}_{\nu',0} W_{\nu,\nu'}^\text{el}, \\
S^\text{vib}_{\nu',0} &= \langle 0' | 1'' \rangle, \\
W_{\nu,\nu'}^\text{el} &= \langle 2A', W_{i,R} | 2A'' \rangle.
\end{align*}$$

(3.2)

The mean LZ transition probability that enters into the expression for the LZ rate coefficient is expressed through the square of the absolute value of the matrix element $W_{i,f}$ on the CL, which is thermally averaged over the rotational (rot) degrees of freedom of the collision complex at fixed values of $R_c(0)$ and $\theta$, $\langle W_{i,f}^{\text{CL}} \rangle^2$. Introducing the dimensionless coupling coefficient $\Xi(0, T)$ defined as

$$\Xi_{i,f}(0, T) = \langle W_{i,f}^{\text{CL}} \rangle^2 \Delta E_{1,0}.$$  

(3.3)

we have

$$\begin{align*}
\Xi_{i,f}(0, T) &= \Xi_{1,0}^{\text{vib}}(0) \Xi_{1,0}^{\text{el}} \Xi_{1,0}^{\text{vib}}, \\
\Xi_{1,0}^{\text{vib}}(0) &= (S^\text{vib}_{\nu',0})^2, \\
\Xi_{1,0}^{\text{el}}(0, T) &= \langle W_{i,f}^{\text{CL}} W_{\nu,\nu'}^{\text{el}} | 2A', A'' \rangle \Delta E_{1,0}^2.
\end{align*}$$

(3.4)

The detailed calculation of $\Xi_{1,0}^{\text{el}}(0, T)$ and $\Xi_{1,0}^{\text{vib}}(0)$ is described in the Appendix, and explicit expressions for $\Xi_{1,0}^{\text{el}}(0, T)$ and $\Xi_{1,0}^{\text{vib}}(0)$ are given by Eqs. (A3), (A4), and (A10).

IV. \textbf{LZ$_{k_{10}}$ RATE COEFFICIENTS FOR NO + Ar COLLISIONS IN A TRANSITION STATE THEORY, SURFACE HOPPING, APPROXIMATION}

Within a transition state theory approach, the rate coefficients $\text{LZ}_{k_{10}}$ are associated with the probability-weighted flux through the dividing surface. The latter corresponds to the surface of revolution generated by the rotation of the crossing line (CL) about the molecular axis. The simplest way for a calculation of $\text{LZ}_{k_{10}}$ is to use the surface hopping (SH) approach. This method, which requires the following of trajectories on both PES, can be simplified in the case of two crossing repulsive PES at the collision energies that are not in a big excess compared to the energy at the crossing line. In addition, the collision energies should not be in too big excess compared with the energy at the crossing line. Then the trajectories do not extend much beyond the crossing line and, near to the CL, can be taken as one-dimensional trajectories normal to the crossing line. This is a version of the reaction-coordinate (RC) approximation that is based on the local separation of variables and the introduction of an effective mass. We take the two-way transition probability in the form of the standard first-order LZ approximation, $P_{1,0}^{\text{LZSH}}(\theta)$, which ignores tunneling transitions and (to be compatible with the SH picture) neglects interference effects by averaging the probability over the Stueckelberg oscillations. In the LZSH approximation, $\text{LZ}_{k_{10}}$ is then identified with $P_{1,0}^{\text{LZSH}}$, the latter being expressed as

$$L_{k_{10}}^{\text{LZSH}} = \frac{1}{2} \int F_{1,0}(0, T) \exp\left[ -\frac{E_c(\theta)}{k_B T} \right] dS(0),$$

(4.1)

where $F(0, T)$ is the mean probability flux

$$F_{1,0}^{\text{LZSH}}(0, T) = \langle v_\theta(0) P_{1,0}^{\text{LZSH}}(0) \rangle,$$

(4.2)

where $v_\theta$ stands for the velocity of the reaction coordinate at the CL, $\langle \ldots \rangle$ signifies the canonical averaging over all dynamical variables except the angular coordinate, and $dS(0)$ is the ring-shaped infinitesimal element of the surface at the CL. The statistical factor 1/2 accounts for the fact that only the approach across one (out of two) PESs leads to relaxation.

With $P_{1,0}^{\text{LZSH}}(\theta)$ being explicitly given by

$$P_{1,0}^{\text{LZSH}}(\theta) = \frac{4 \pi W_{1,0}^{\text{CL}} | W_{1,0}^{\text{CL}} | R - R_c(0) |}{v_\theta(0) | \text{grad} V(R, 0) |}$$

(4.3)

the thermal averaging of the probability flux in Eq. (4.2) reduces to the thermal averaging of $|W_{1,0}^{\text{CL}}|^2$. The integrand in Eq. (4.1) can be simplified once one realizes that $dS(0)$ is proportional to grad$V(R, 0)$ on the CL. This finally yields

$$L_{k_{10}}^{\text{LZSH}} = \frac{\pi}{k_B T} \int_0^\pi 4 \pi^2 W_{1,0}^{\text{CL}}|W_{1,0}^{\text{CL}}|^2 \exp\left[ -\frac{E_c(\theta)}{k_B T} \right] R_c^2(0) \sin\theta d\theta.$$  

(4.4)

A useful approximation to $L_{k_{10}}^{\text{LZSH}}$ is obtainable if one considers the case when the main contribution to the integral in Eq. (4.4) comes from a small region of $\theta$ near $\theta_0$, where $E_c(\theta)$ has a deep minimum (which is a standard approximation in the transition state theory approach). Within this region,
one uses the quadratic approximation to $E_a(0)$ [see Eq. (2.3)]. Neglecting the $\theta$ dependence of all terms in the integrand in Eq. (4.4) except the leading exponential, we obtain an explicit expression for $LZ\mu_{1,0}^{SH}(T)$ that arises from the window of effective configurations near the optimal configuration defined by $R_a, \theta_a,$

$$LZ\mu_{1,0}^{SH} = \frac{2\Delta E_{1,0} \Xi_{1,0}((0, \theta), T)}{\hbar \omega_c((0, \theta))} \times 2\pi R_a^2 \sin \theta_a \sqrt{\frac{2\pi k_B T}{E_a^{(2)}}} \times \exp(-E_a/k_B T).$$  

(4.5)

In this expression, the separated factors have the following significance:

(i) the flux-weighted canonically averaged LZSH transition probability for the radial motion at the optimal configuration,

(ii) the cross section in the form of a spherical element for a window of effective configurations,

(iii) the Arrhenius exponent for attaining the optimal configuration.

Equation (4.5) leads to the following detailed temperature dependence of $LZ\mu_{1,0}^{SH}(T)$, as expressed through the molecular parameters of the free NO molecule $M, r_e, A$ and the parameters of the NO–Ar collision complex in the optimal configuration, $\mu, R_a, \alpha_a, \theta_a, E_a, E_a^{(2)}$,

$$k_{1,0}^{LZSH} = D_{10} \left( \frac{T}{T_{SO}} + 1 \right) \times \left( \frac{T}{T_a} \right)^{1/2} \times \exp(-T_a/T),$$  

(4.6)

where $T_a = E_a/k_B = 5250$ K,

$$T_{SO} = \frac{A^2}{4} \left( \frac{\hbar^2 k_B}{M r_e^2 \sin^2 \theta_a} + \frac{\hbar^2 k_B}{\mu R_a^2 \sin^2 \theta_a} \right)^{-1} = 3021, \text{ K},$$

$$D_{10} = \frac{\pi \Xi_{1,0}^{vb}(0, \alpha_a) \hbar^2}{\hbar E_a \alpha_a(\theta_a)} \pi R_a^2 \sin \theta_a \sqrt{ \frac{2\pi E_a^{(2)}}{E_a^{(2)}} } \times 2.23 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} = 1.34 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$  

(4.7)

The three temperature-dependent factors in Eq. (4.6) correspond to the factors (i)–(iii) given above, where the first with (i) expresses the interplay between the Coriolis and spin–orbit interactions inducing the nonadiabatic transition. We note in passing that this interplay, in the optimal collision complex configuration of NO–Ar, represents a counterpart to the intermediate $a$–$b$ Hund coupling case of a free NO molecule.

The accuracy of the optimal-configuration approximation can be characterized by the ratio $\frac{LZ\mu_{1,0}^{SH}(T)}{LZ\mu_{1,0}^{SH}(T)} \equiv f_{1,0}^{LZSH}(T)$. It is expected to be slightly below unity since the quadratic approximation for $E_a(\theta)$ produces a slightly broader width; see Fig. 3. A plot of $f_{1,0}^{LZSH}(T)$ is presented in Fig. 4. The values of $f_{1,0}^{LZSH}(T)$ from this plot, together with the analytical representation of $LZ\mu_{1,0}^{SH}$ from Eq. (4.6), define $f_{1,0}^{LZSH}$ as

$$LZ\mu_{1,0}^{SH}(T) = f_{1,0}^{LZSH}(T) \times LZ\mu_{1,0}^{SH}(T).$$  

(4.8)

V. QUANTUM CORRECTIONS TO LZSH RATE COEFFICIENTS

A calculation of $LZ\kappa_{1,0}(T)$ in the LZSH approach ignores interference effects for overbarrier transitions and tunneling effects for underbarrier transitions. As suggested in Refs. 17 and 18, these two quantum effects are represented by a correction factor in the rate coefficient. Here, the latter is calculated in the uniform Airy (UAi) approximation that permits one to represent $LZ\kappa_{1,0}(T) = LZ\kappa_{1,0}^{UAi}(T)$ as

$$LZ\kappa_{1,0}^{UAi} = C_{1,0}^{UAi}(A) \times LZ\mu_{1,0}^{SH}(T),$$  

(5.1)

where $A$ denotes the Arrhenius ratio $A = E_a/k_B T$ and $C_{1,0}^{UAi}(T)$ is defined as

$$C_{1,0}^{UAi}(A) = \int_{\varepsilon_0}^{\varepsilon_1} R^{UAi}_{1,0}(\varepsilon) \exp(-A(\varepsilon - 1)) d\varepsilon,$$

(5.2)

where $\varepsilon$ is the scaled energy, $\varepsilon = E/E_a$, and $R^{UAi}_{1,0}(\varepsilon) = P^{UAi}_{1,0}(\varepsilon)/P^{UAi}_{1,0}(\varepsilon)$ are the probability ratios that do not depend on the coupling strength. Within this definition, the LZSH probability $P^{SH}_{1,0}(\varepsilon)$ is related to the high-energy asymptote (As) of $P^{UAi}_{1,0}(\varepsilon)$ averaged over the Stueckelberg (St) interference oscillations, i.e.,

$$P^{SH}_{1,0}(\varepsilon) = \langle A(\varepsilon) \rangle_{\text{St}}.$$  

(5.3)

Graphs of $P^{UAi}_{1,0}(\varepsilon)$ and $R^{SH}_{1,0}(\varepsilon)$ are calculated for reaction-coordinate sections of the ab initio PESs and the effective mass $\mu^* = 9.43$ amu ($\mu^* = 0.55\mu$, $\mu = 17.14$ amu), as recommended in Refs. 17 and 18. The results are shown in Fig. 5.

One observes that the width of the first Stueckelberg maximum of the transition probability, as calculated within the UAi approach, corresponds to about $E_a/k_B = 5250$ K. This casts doubts on the applicability of the LZSH approximation for temperatures below, say, 5000 K as it lacks the averaging over Stueckelberg oscillations. The standard LZ formula (without
averaging) also cannot be applied since the LZ probability diverges below the first Stueckelberg maximum (because of the breakdown of the WKB approximation).

The plot of \( C^{UAi}(A) \) vs \( A \) across the range of 0.5 < \( A \) < 6, covering the temperature range of 900 < \( T \) < 2000 K of Ref. 19, is shown in Fig. 6, together with its partial contributions, \( C^{UAi+}(A) \) and \( C^{UAi-}(A) \) from underbarrier and overbarrier transitions.

As expected, for low values of \( A \), \( A < 1 \), \( C^{UAi}(A) \) is very close to unity, indicating good performance of the LZSH approximation with only a small relative contribution from underbarrier transitions. On the other hand, a small deviation in \( C^{UAi}(A) \) from unity (say 10% at \( A = 3.5 \)) does not necessarily indicate a small quantum effect in the nonadiabatic dynamics: at this value of \( A \), the underbarrier and overbarrier transitions both make comparable contributions to \( C^{UAi}(A) \). A relatively small quantum correction for \( A < 4 \) appears rather unexpected considering the very different energy dependences of \( R^{UAi+}(\varepsilon) \) and \( R^{UAi-}(\varepsilon) \). It indicates that good performance of the LZSH approximation does not necessarily imply negligible quantum effects in the nonadiabatic dynamics. For \( A > 6 \), the correction factor \( C_{1,0}^{UAi}(A) \) merges with its tunneling Landau-Lifshitz counterpart discussed in detail in Refs. 17 and 18.

VI. COMPARISON OF THEORETICAL RESULTS WITH EXPERIMENTAL DATA: INTERPLAY OF LZ AND LT PATHWAYS

A comparison of the theoretical values of \( LZk_{1,0} \) with the available experimental data requires an estimate also of the contribution from the LT relaxation pathway. We, therefore, represent the overall rate coefficient \( k_{1,0} \) as

\[
k_{1,0} = LZk_{1,0} + LTk_{1,0}.
\]

A rough estimate of \( LTk_{1,0} \) is sufficient to determine the temperature range, where \( LZk_{1,0} \) dominates, and to discuss the interplay of the LZ and LT relaxation pathways. This estimate can be made by rescaling the Schwartz–Slausky–Herzfeld (SSH) rate coefficient\(^{5,6} \) for a reference system that resembles NO–Ar (in the electronic structure of the diatom and the masses of the atoms) and for which ample experimental data exist. In this way, we represent \( LTk_{10} \) by the SSH expression, \( LTk^{SSH}_{10}(T) \), in the form \(^{27–30} \)

\[
LTk^{SSH}_{10}(T) = A^{SSH}(T) \exp\left(\frac{(3/2)(T^{LT}/T)^{1/3}}{+ T_{V}/2T}\right).
\]

Here, the exponent is the classical LT term and its first WKB correction with \( T_{V} = \Delta E_{10}/k_{B} \), while the SSH pre-exponential factor \( A^{SSH}(T) \) is proportional to \( T^{1/3} \), i.e., \( A^{SSH}(T) = C^{SSH}T^{1/3} \). \( LTk^{SSH}_{10}(T) \) is then characterized by two temperature-independent parameters, \( T^{LT} \) and \( C^{SSH} \). The values of these parameters are determined by a fit of Eq. (6.2) to the experimental data. We have chosen the \( O_{2}–Ar \) system as reference because it has particle masses close to those of NO–Ar and there exists a wealth of experimental data (1200–4000 K).\(^{31–34} \) Besides, \( O_{2} \) resembles NO in its electronic structure and in its interaction with Ar (the outer shell of \( O_{2} \) has two electrons occupying the \( 1\pi_{g} \) MO, while a single electron of NO occupies the \( 2\pi \) MO; the electronic configuration \( 1\pi_{g}^{2} \) produces a \( X^{1\Sigma_{g}^{+}} \) ground electronic state with the particular electronic occupation \( 1\pi_{g}^{1}1\pi_{u}^{0} \), prime and double prime denoting the reflection symmetry with respect to an arbitrary plane passing through the molecular axis). Arguments of the asymptotic approach then indicate that the interaction of Ar with \( O_{2}(X^{1\Sigma_{g}^{+}}, 1\pi_{g}^{1}1\pi_{u}^{0}) \) will resemble that of Ar with NO(\( X^{3\Pi_{1,2}}, 2\pi^{0} \)), where now the plane of reflection is identified with the system plane. In other words, the single BO PES of \( O_{2}–Ar \), \( V(R, 0) \), will be similar to \( V'(R, 0) \) for NO–Ar, except for a small angular anisotropy in the latter case. We, therefore, identify \( LTk_{10}(NO–Ar) \) with a scaled rate coefficient \( LTk^{SSH}_{10}(O_{2}–Ar) \) (we tolerate possible effects of the small anisotropy and also the difference between the SSH rate coefficients on the \( V'(R, 0) \) and \( V'(R, 0) \) PES for the NO–Ar collisions). The scaling of \( LTk_{10}(O_{2}–Ar) \) to \( LTk^{SSH}_{10}(NO–Ar) \) uses the dependence of \( T^{LT} \), \( T_{V} \), and \( A^{SSH} \) on the vibrational frequency.
of the diatomic molecule, \(33-36\) i.e.,

\[
A^{SSH} \propto \omega^{4/3}, \quad T^{LT} \propto \omega^{2}, \quad T_V \propto \omega^{0}.
\]

The performance of the SSH fit to the experimental data for \(O_2\text{–Ar}\) relaxation is demonstrated in Fig. 7 [where also the scaled \(LT_{1,0}^{SSH}(\text{NO–Ar})\) is included]. Also shown are linear LT plots fitted to the high-temperature rate coefficients (dashed blue and green lines).

The values of the parameters essential in the scaling are listed in Table II.

Plots of the LZ rate coefficients \(LT_{1,0}^{KUAi}\) and \(LT_{1,0}^{SSH}\), LT rate coefficient \(LT_{1,0}^{SSH}\), and total rate coefficients for the NO–Ar system in Fig. 8 are compared with the available experimental data.

The following conclusions can be drawn from above:

(i) The LZ pathway dominates the relaxation rate at \(T < 2500\) K; i.e., here one has \(LT_{1,0}^{KUAi} \gg LT_{1,0}^{SSH}\).

(ii) At the low-temperature end of the shown range, the rate coefficient \(LT_{1,0}^{KUAi}\) notably deviates from its \(LT_{1,0}^{SSH}(T)\) counterpart. This is explained by the contribution of tunneling to the nonadiabatic transitions. Below about 900 K (not shown in Fig. 8 but discussed in detail in Refs. 17 and 18), this deviation strongly increases.

(iii) At a temperature near 3500 K, \(LT_{1,0}^{KUAi}\) and \(LT_{1,0}^{SSH}\) approach each other, and for \(T < 3500\) K, the LT pathway dominates the relaxation rate.

(iv) The calculated LZ relaxation rates are in reasonable agreement with the experimental data for \(T < 2500\) K, i.e., in the range where \(LT_{1,0}^{KUAi} \gg LT_{1,0}^{SSH}\).

We further compare theory and experiment for the example of 1500 K, where we illustrate the contribution of different factors to the expression for \(LT_{1,0}^{KUAi}\), see Eqs. (4.8) and (5.1). At this temperature, \(C_{1,0}^{KUAi} \approx 1.1\) and \(f_{1,0}^{SSH} \approx 0.9\), such that the two factors nearly compensate. Then, Eq. (5.1) gives \(k^{CC}(T)\mid_{T=1500K} = 3.17 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) (or 5.27 \(\times 10^{-15}\) cm\(^3\) s\(^{-1}\)). The experimental counterpart of this quantity, as recovered from the state-specific effective rate coefficient \(k(1)\mid_{T=1500K} = 3.0 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) (reported in Table I of Ref. 19), is \(k^{exp}(T)\mid_{T=1500K} = 2.8 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) (or 4.06 \(\times 10^{-15}\) cm\(^3\) s\(^{-1}\)).

Considering the approximations inherent in the asymptotic estimation of the theoretical coupling coefficient and the error limits \(\pm 30\%\) of the measured rates, the agreement between experiment and theory appears quite satisfactory. We also note that Coriolis and spin–orbit interactions at this temperature make comparable contribution to the nonadiabatic coupling, with the latter dominating at lower temperatures.

**VII. CONCLUSIONS**

The inelastic scattering of NO(\(2\Pi_2\)) with noble gas atoms has emerged as the paradigm for nonadiabatic collisions of open-shell molecules. Rotationally inelastic collisions have been treated extensively in experiment and
theory (see, e.g., Ref. 36 for NO–Ar collisions). The situation for vibrationally inelastic collisions of NO(3Πu 1) with noble gas atoms, because of the larger number of open channels (theory) and extremely small values of the inelastic cross sections (experiment), is much more complicated. Therefore, here we adopted a reaction-coordinate approach within the classical approximation for electronically nonadiabatic dynamics, using a canonical distribution over the dynamical variables. This approach appeared appropriate for the interpretation of experimental studies of NO relaxation in shock-heated Ar and for an extension of the theoretical approximations for further application to similar processes. This extension became possible because an appropriate electronic potential surface for the NO–Ar system and an asymptotic method for the estimate of the exchange interaction in nonadiabatic coupling are available. Non-adiabatic transition probability in the uniform Airy approximation 21 shows pronounced quantum effects for overbarrier (interference) and underbarrier (tunneling) regimes across the energy range which is essential for the calculation of thermally averaged rate coefficients at several thousand K and below. This approach well reproduces experimental rate coefficients under shock wave conditions at about T = 1500 K. Rather unexpectedly, a quite similar result is obtained within the surface-hopping approximation, which ignores the quantum effects. This peculiarity is related to a unique feature of the linear LZ model: the equivalence of the quantum and the semiclassical treatments. 24

Since the theory explicitly predicts the temperature dependence of $L_{2}k_{10}$, extrapolations toward higher and lower temperatures can be made. For higher temperatures, it predicts a crossover of $L_{2}k_{10}$ and $L_{3}k_{10}$ rate coefficients and for lower temperatures it demonstrates incipient tunneling effects.

Acknowledgments

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Appendix: Calculation of the Coupling Coefficients $\Xi_{A^{'},A}(0,T)$ and $\Xi_{V,0}(\theta)$

1. Coupling coefficient $\Xi_{A^{'},A}(0,T)$

The matrix element $W_{A^{'},A}(\theta) = \langle \phi_{A^{'},A}(\theta) | \phi_{A}(\theta) \rangle$ is calculated for a rotating rigid collision complex AB-X with fixed coordinates R, $\theta$, $r = r_{c}$ 26 (see also Ref. 26 and Sec. 7 of Ref. 8). The rotation is described by the asymmetric top Hamiltonian $H_{AB}(J, P_{y}, \theta)$ of the form

$$H_{AB}^{AT}(J, P_{y}, \theta) = \frac{P_{y}^{2}}{2(I_{r} + I_{K})} + \frac{\cos^{2}(\psi_{K}) + \cos^{2}(\psi_{K} + \theta)}{2I_{r}} \left( J^{2} - P_{y}^{2} \right) \cos \theta,$$

where $I_{r} = Mr^{2}$ and $I_{K} = \mu R^{2}$ with the reduced masses $M$ and $\mu$ of the AB molecule and the AB-X pair, respectively. The dynamical variables in Eq. (A1) are the total angular momentum $J$ of the AB-X system, its projection $P_{y}$ onto the normal to the AB plane, and the angle $\psi_{K}$ (conjugate to $P_{y}$ and counted from the projection of $J$ onto the system plane) that describes the planar rotation of the ABX system. We note in passing that $H_{AB}$ does not include $\psi_{r}$ and $\psi_{K}$ (because of the free rotation of the AB-X system and the isotropic orientation of the total angular momentum vector in space). Particular cases of the AsT Hamiltonian $H_{AB}^{AT}$ in Eq. (A1) are the Hamiltonian $H_{AB}^{OST}$ of an oblate symmetric top (for $I_{r} = I_{K}$, $\theta = \pi/2$) and the Hamiltonians $H_{AB}^{S}$ of linear rotors (for $I_{r} = 0$, $\psi_{K} = \pi/2$ and for $I_{K} = 0$, $\psi_{K} + \theta = \pi/2$).

With the explicit expression for $o_{a} = o_{a}(J, P_{y}, \psi_{K}; R, \theta)$ (see Ref. 8), the rotational averaging of $[W_{A^{'},A}(\theta)]^{2}$ is performed with the Hamiltonian in Eq. (A1) over the phase space $J, \psi_{r}, \psi_{K}, P_{y}, \psi_{K}$. In this way, the quantity $\Xi_{A^{'},A}(0,T)$ assumes the form (Ref. 8, Sec. 20)

$$\Xi_{A^{'},A}(0,T) = \frac{\hbar k_{B} T}{\Delta E_{10}^{2} I_{r}} \cot^{2} T + \frac{\hbar k_{B} T}{\Delta E_{10}^{2} I_{r}} \sin^{2} \Delta \theta \sin^{2} \Delta \theta + \frac{A^{2}}{4\Delta E_{10}^{2}}.$$  

(A2)

The first two terms of the rhs of Eq. (A2) originate from $[o_{a}(J, P_{y}, \theta)]^{2}$ [i.e., from the first term of the rhs of Eq. (3.1)]. They are related to the Coriolis interaction between the $2A''$ and $2A'$ electronic states, which is induced by the rotation of the N–O–Ar plane of the asymmetric top N–O–Ar. The third term arises from the spin–orbit coupling between the $2A''$ and $2A'$ electronic states. With known values of the molecular parameters $M$, $r_{c}$, $A$ and the collision complex parameters $\mu$, $R_{0}$, $\theta$, Eq. (A2) gives the temperature dependence of $\Xi_{A^{'},A}(0,T)$ as

$$\Xi_{A^{'},A}(0,T) = \frac{A^{2}}{4\Delta E_{10}^{2}} \left( \frac{T}{T_{SO/Cor}(0)} + 1 \right).$$  

(A3)

$$T_{SO/Cor}(0) = \frac{A^{2}}{4} \left( \frac{\hbar k_{B} T}{I_{r}} \cot^{2} \Delta \theta \sin^{2} \Delta \theta + \frac{\hbar k_{B} T}{I_{r}} \sin^{2} \Delta \theta \sin^{2} \Delta \theta \right)^{-1}.$$  

(A4)

We note that the ratio of the second term to the first term in Eq. (A4), at the optimal NO–Ar configuration, is equal to 0.29. If the second term in Eq. (A4) is neglected, then the Coriolis interaction originates from the rotation of the N–O–Ar plane about the space-fixed R axis or, what is the same, from the rotation of the NO molecule about $R$. Asymptotically, when $\Delta V \rightarrow 0$, this interaction is responsible for the transformation of the coupled linear rotor states $| j, m, A \rangle, A = A', A''$ into uncoupled symmetric top states $| j, m, \Lambda \rangle, \Lambda = \pm \Lambda$. Finally, the latter can be transformed into the definite parity states $| j, m, \Lambda(A') \rangle, A = A', A''$, where $\Lambda(A')$, $\Lambda(A'')$ now correspond to different reflection symmetries of the electronic states in the plane of rotation of a free diatom. 25, 38 The molecular parameters, which enter into Eqs. (A3) and (A4) and are taken from Ref. 39, are listed in Table III.

2. Coupling coefficient $\Xi_{V,0}(\theta)$

The vibrational overlap integral $S_{V,0}^{\text{ vib}} = \langle 0 | 1'' \rangle$ between the vibrational functions supported by the potentials

$$S_{V,0}^{\text{ vib}} = \langle 0 | 1'' \rangle.$$
TABLE IV. Parameters (in a.u.) of the NO(\(ν = 0\), \(J = 0\)) states.

<table>
<thead>
<tr>
<th>(M)</th>
<th>(μ)</th>
<th>(r_e)</th>
<th>(A)</th>
<th>(A^2/ΔE_{10})</th>
<th>(\bar{r}^\text{SOCl}_0(\theta_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.47 amu</td>
<td>17.14 amu</td>
<td>2.175 (a_0)</td>
<td>121 cm(^{-1})</td>
<td>1.040 (10^{-3})</td>
<td>3021 K</td>
</tr>
<tr>
<td>1.36-10(^4) (m_e)</td>
<td>3.125-10(^4) (m_e)</td>
<td>5.51-10(^{-4}) a.u.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(U(r, R, 0)\) and \(U''(r, R, 0)\) is calculated for the non-rotating rigid collision complex AB-C with fixed coordinates \(R, 0\) and the oscillating coordinate \(r\). A general analytical expression for \(S^{\text{vib}}_{ν',ν}\) is known for harmonic and Morse oscillators in terms of the \(ν\)-dependent potentials (see, e.g., Ref. 40, Sec. 4.8). In turn, the latter should be expressed through the parameters of the potentials \(U(r, R, 0)\) and \(U''(r, R, 0)\) on the CL. In our case (according to Ref. 22), \(U'(r, R, 0)\) and \(U''(r, R, 0)\) can be considered as perturbations on the background of the NO intramolecular potential \(U_0(r)\) that supports the zero-order vibrational states \(q^{ν}_{\nu'}(r)\).

Then, \(S^{\text{vib}}_{ν',ν}(r, \theta)\) assumes the form

\[
S^{\text{vib}}_{ν',ν}(r, \theta) = \frac{(r - r_0)_{01}}{ΔE_{10}} \left( \frac{∂}{∂r} U(r, R, 0) \right)_{r = r_e, R = R_0},
\]

\[
ΔU(r, R, 0) = U_{ν'}(r, R, 0) - U_{ν}(r, R, 0),
\]

where \((r - r_0)_{01}\) is the matrix element calculated with the zero-order vibrational functions of the \(X^+Π\) state of NO, i.e., \((r - r_0)_{01} = \sqrt{8M}/\sqrt{2M_0}\). For the description of the \(r\) dependence of \(ΔU\), we adopt the asymptotic theory of the exchange interaction as suggested in Ref. 8 and used earlier in the same context. Within the asymptotic approach, the main dependence of \(ΔU(r, R, 0)\) on \(r\) arises from the exponential factor that, when written in a.u., reads as

\[
ΔU(r, R, 0) \propto \exp(-\sqrt{2I_{NO}(r)}R),
\]

where \(I_{NO}(r)\) is the ionization potential of the NO(\(X^+Π\)) molecule at the internuclear distance \(r\). Substituting \(ΔU\) from Eq. (A6) into Eq. (A5), in this approximation, we obtain for \(S^{\text{vib}}_{ν',ν}(\theta)\) the expression

\[
S^{\text{vib}}_{ν',ν}(\theta) = (r - r_0)_{01}R_0(\theta) \left( d\sqrt{2I_{NO}(r)}/dr \right)_{r = r_e},
\]

The function \(I_{NO}(r)\) is recovered from the potentials \(U^{\text{X+Π}}_{ν} (r)\) and \(U^{\text{X+Π}}_{ν'} (r)\) of the electronic ground states \(X^+Π\) and \(X^+Π\) of the ion and the neutral, respectively, i.e.,

\[
I_{NO}(r) = U^{\text{X+Π}}_{ν} (r) - U^{\text{X+Π}}_{ν'} (r).
\]

The linear part of the \(r\) dependence of \(I_{NO}(r; X^+Π)\) near \(r = r_e\) arises from that of the parabolic potential curve of \(NO(3H^2Π)\),

\[
U_{NO}(r; X^+Π) = M(ω^+)^2(r - r^*_e)^2/2,
\]

where \(ω^+\) and \(r^*_e\) are the parameters of \(NO^+\). Then,

\[
dI_{NO}(r)/dr|_{r = r_e} = M(ω^+)^2(r_e - r^*_e).
\]

In this approximation, the expression for \(\Xi^{\text{vib}}_{1,0}(0)\) assumes the form

\[
\Xi^{\text{vib}}_{1,0}(0) = \left( S^{\text{vib}}_{ν',ν}(0) \right)^2,
\]

\[
S^{\text{vib}}_{ν',ν}(\theta) = \sqrt{8/\overline{M}_0R_0(\theta)} \left( M(ω^+)^2(r_e - r^*_e) \right) / \sqrt{2I_{NO}(r_e)},
\]

where the numerical values of the parameters are listed in Table IV. The \(θ\) dependence of \(S^{\text{vib}}_{ν',ν}(0)\) here enters only through \(R_0(θ)\). Referring to Fig. 1, we see that within the angular sector marked in this figure, \(\Xi^{\text{vib}}_{1,0}(0)\) varies less than about 20%. In particular, for \(θ = 0°\), Eq. (A10) yields \(\Xi^{\text{vib}}_{1,0}(0) = 1.10 \cdot 10^{-2}\).
