Chapter 2

On the Theory of the Reaction Rate of Vibrationally Excited
CO Molecules with OH Radicals

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On the theory of the reaction rate of vibrationally excited CO molecules with OH radicals
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The dependence of the rate of the reaction CO+OH→H+CO₂ on the CO-vibrational excitation is treated here theoretically. Both the Rice-Ramsperger-Kassel-Marcus (RRKM) rate constant \( k_{RRKM} \) and a nonstatistical modification \( k_{non} \) are used in the analysis. The experimentally measured rate constant shows an apparent increase at low CO-vibrational temperatures, reflecting the actual energy barrier that increases when \( v \) is increased further. This results can be regarded as a prediction when \( v \) state-selected rate constants become available.

I. INTRODUCTION

The conversion of CO to CO₂ by reaction with an OH radical is one of the principal oxidation reactions in the atmosphere and has been the subject of many experimental and theoretical studies. The currently accepted reaction mechanism involves a CO and OH bimolecular association to form a vibrationally excited trans-HOCO radical, followed by a cis-trans isomerization. There are also the back reaction to reform the reactants, the forward reaction leading to H+CO₂ and the collisional stabilization of HOCO. In the presence of oxygen both the H+CO₂ and the stabilized HOCO form the same products, HO₂ and CO₂.

The non-Arrhenius behavior for the thermal rate constant has been extensively studied in experiments and theory. It involves a nearly activationless barrier in the entrance channel \( CO + OH \rightarrow HOCO \) and also in the exit channel \( HOCO^+ \rightarrow H + CO_2 \). There is a large H-tunneling effect in the latter, and at low temperatures there is even tunneling in the former. In the Arrhenius plot of ln \( k_{rate} \) vs 1/T the slope increases significantly at temperatures higher than 500 K, reflecting the actual energy barrier that exists when H-tunneling becomes less important.

In a novel experiment Dreier and Wolfhram formed vibrationally excited CO molecules by collision of CO with vibrationally excited N₂. The latter was obtained by microwave discharge in an N₂/Ar mixture to form excited N⁺(S), which then reacted with NO. The vibrational temperature \( T_v \) of the CO molecules was determined from the optical absorption spectrum of the vibrational-rotational states of CO\( (v,J) \) at or below 1800 K. On the other hand, the rotational and translational temperatures remained at room temperature. The OH radicals were obtained from a discharge in H₂/Ar to yield H, which then further reacted with NO₂ to form OH.

Under these conditions the rate constant appeared to decrease by about 15% from its room-temperature value when \( T_v \) was increased to 1800 K, though with large error bars (the results of many measurements). We treat this behavior in the present article and make predictions for \( v \) state-selected experiments, where the effects would be considerably larger.

The calculational method is summarized in Sec. II, and the results are given and discussed in Sec. III.

II. THEORY AND CALCULATION METHOD

The key aspects of the calculations are noted below, with more details being given in the earlier paper.

A. Kinetic scheme and rate constants

Because the energy barrier between cis- and trans-HOCO is much lower than the energy barriers in the entrance and exit channels, we can assume as before that the cis and trans energetic intermediates HOCO⁺ easily interconvert. The pressure in the experiments was about 4 mbars, and so collisional stabilization by bath gases can be neglected. At zero pressure, the kinetic scheme for the vibrationally excited CO molecules reacting with the OH radicals at an energy \( E \) and total angular momentum \( J \) is given by

\[
\text{CO}^v(J) + \text{OH} \rightarrow \text{HOCO}^+(EJ),
\]

and

\[
\text{HOCO}^+(EJ) \rightarrow \text{CO} + \text{OH},
\]

where \( v \) is the CO vibrational quantum number, \( E \) is the energy of the CO molecules, and \( k_{rate} \) is the rate constant for the reaction.
$$\text{HOCO}^* (E_J) \rightarrow \text{H} + \text{CO}_2.$$  

The rate constant for the forward reaction in Eq. (1) is denoted by $k_v (E_J)$, where $v$ is a vibrational quantum number. The rate constant $k_v (E_J)$ in Eq. (2) yields CO having any CO vibrational quantum number and not necessarily having the initial $v$. The rate constants $k_v (E_J), k_{v-1} (E_J)$, and $k_{v+1} (E_J)$ are $E$ and $J$ dependent. The limiting low-pressure steady-state rate constant $k^v$ for any specified initial CO vibrational quantum state $v$ is given by

$$k^v = \sum_{E} \int \frac{k_v (E_J) k_{v+1} (E_J)}{k_v (E_J) + k_{v+1} (E_J)} dE.$$  

In terms of numbers of quantum states of the two transition states, this low-pressure rate constant at any given $v$ is

$$k^v = \sum_{E} \int \frac{N_v (E) N_{v+1} (E)}{h \Omega [N_v (E) + N_{v+1} (E)]} dE,$$  

where $Q$ is the partition function of the OH and CO when CO is in the specified initial vibrational state $v$. $N_v (E), N_{v-1} (E),$ and $N_{v+1} (E)$ denote the sums of quantum states of the transition states for the entrance at specified $v$, entrance at all accessible $v$'s, and exit channels, respectively, for the energy $E$ and total angular momentum $J$. When $v \geq 1$, the $N_v (E)$ for the backward reaction in the entrance channel is larger than $N_v (E)$ because the energy redistribution in the intermediate HOCO$^*$ yields a large number of quantum states in $N_v (E)$. Each sum of states includes a tunneling correction for a microcanonical ensemble $^{33,34}$

$$N_i (E) = \int_{E_{\text{min}}}^{E} \kappa_i (E') \rho_i ((E - E')J) dE' \quad (i = 1, 2)$$  

and

$$N'_i (E) = \int_{E_{\text{min}}}^{E} \kappa_i (E') \rho'_i ((E - E')J) dE',$$  

where $E_{\text{min}}$ denotes the energy minimum in HOCO$^*$. In Eq. (7) for $N'_v (E)$, unlike Eq. (7) for $N_v (E)$ and $N_{v-1} (E)$, only an energy $E - \nu \Delta v$ is available for energy redistribution in the $\nu'_i$ in this transition state. We note that for the $E$ in $N'_v (E)$ in Eq. (7) one writes $E - \nu \Delta v$. The rate constant at the vibrational temperature $T_v$ is then given by

$$k(T_v) = \frac{1}{Q_{CO} (T_v)} \sum_v k^v \exp \left( - \frac{\nu \Delta v}{k_b T_v} \right),$$  

where $Q_{CO} (T_v)$ is the vibrational partition function of the CO molecules at a vibrational temperature $T_v$. The potential-energy surface used is the same as that employed in the earlier paper, with the same two adjusted parameters and the same refined vibrational frequencies of all stationary structures. In the calculation the number of quantum states of the internal rotation about the HO–CO bond in the entrance channel was treated as before as a one-dimensional hindered rotor.

### B. Nonstatistical modification of RRKM

We recall previous studies where the reaction CO+OH $\rightarrow$ CO$_2$+H showed a nonstatistical behavior $^{35-40}$ in both bulk gas-phase and molecular-beam studies of the reverse reaction, H+CO$_2$ $\rightarrow$ OH+CO. It was observed that the vibrational excitation of the CO product of that reaction was below that expected from statistical theory for the HOCO$^*$ intermediate. There appear to be various nonstatistical components. In the present nonstatistical modification of the Rice-Ramsperger-Kassel-Marcus (RRKM) theory, as in Ref. 28, we simply assume that the intramolecular energy transfer between the high-frequency OH-stretching vibration in the HOCO$^*$ and the other (lower-frequency) modes is not rapid enough to yield an intramolecular statistical distribution during the typical lifetime of the HOCO$^*$ before the latter dissociates into H+CO$_2$.

In our earlier study $^{28}$ a nonstatistical modification of the RRKM theory was also used to treat the reaction, a treatment which included H- and C-isotope effects. The nonstatistical modification removed an existing discrepancy in the literature $^{26,41}$ between results of experiment and the RRKM theory for the H/D-isotope effect at low pressures. It reproduced the non-Arrhenius behavior for the rate constants at high and low temperatures.

In this nonstatistical modification $^{28}$ of the RRKM theory, it was assumed that only a limited amount of energy $\xi$ can be transferred into or out of the OH-stretching vibration just before the HOCO$^*$ enters the transition state $T_{S_2}$, from which it dissociates into H+CO$_2$. That is, there is restricted energy transfer between the HOCO$^*$ phase space and the phase space of $T_{S_2}$, as depicted schematically in Fig. 1 for the reverse reaction. The value assumed $^{28}$ for $\xi$, 4000 cm$^{-1}$, is a little larger than the energy of one OH-stretching quantum. Therefore, the amount of energy in the H-dissociation motion in the $T_{S_2}$ produced from an intermediate HOCO$^*$ with $n$ quanta in the OH vibration is limited in $T_{S_2}$ to an energy in $n \nu \Delta v \pm \xi$ interval, as shown in Fig. 2. The dissociation rate constant $k_J (E)$ at a total energy $E$ and angular momentum $J$ of HOCO$^*$ thus includes a partitioning over the quantum number $n$ of the OH-stretching vibration in
The allowed values of \( n \) are 0, 1, \ldots, \( n_{\text{max}} \), a total of \( (n_{\text{max}}+1) \) values, where \( n_{\text{max}} \) is the maximum allowed quantum number of the OH-stretching vibration in the HOCO' at the given \( E \) and \( J \). The \( N_2(EJ) \) in Eq. (5) is thus replaced by the weighted sum,

\[
N_2^{\text{non}}(EJ) = \frac{1}{(n_{\text{max}}+1)} \sum_{n=0}^{n_{\text{max}}} N_2^0(EJ),
\]

where in virtue of the definition of \( \xi \) we have

\[
N_2^0(EJ) = \int_{E_0}^{E_{\text{max}}(EJ)} \frac{E_0}{\hbar \nu} \frac{\rho^0(EJ)}{\rho(EJ)} \, dE'.
\]

The \( \kappa(E') \) and \( \rho^0(E-E')J \) are the same as those in Eq. (6), \( \nu \) in Eq. (10) is the OH-stretching frequency of cis-HOCO, and the lower and upper bounds of \( E \) are as indicated. \( E_0 \) is the potential energy plus the zero-point energy in HOCO'. The upper and lower bounds of \( E \) in Eq. (10) limit the amount of energy \( \xi \) transferring between other modes and the OH-stretching motion in TS2. When \( \xi \) approaches infinity, the energy transfer between modes is much faster than the lifetime of intermediates and the number of states used in the conventional RRKM is obtained at any \( n \), i.e., \( N_2^0(EJ) = N(J) \).

Using Eq. (9) and the rate constants \( k_2(J) \) for the reaction from the intermediate HOCO' with \( n \) quanta in the OH-stretching mode, the conventional RRKM rate constant at specified \( E \) and \( J \) can be expanded as

\[
k(EJ) = \frac{N(J)}{\hbar \rho(EJ)} = \frac{1}{n_{\text{max}}+1} \sum_{n=0}^{n_{\text{max}}} \rho^0(EJ) \kappa_2^n(EJ),
\]

since \( \kappa_2(E') = \kappa_2^0(EJ)/\hbar \rho^0(EJ), \) where \( \rho^0(EJ) \) is the density of states of the HOCO' at OH vibrational state \( n \). Equation (11) is Eq. (C3) (Ref. 42) in Ref. 28. The rate constant with nonstatistical modification can be obtained by using Eqs. (10) and (11) with a finite value of \( \xi \).

### III. RESULTS AND DISCUSSION

The calculated rate constants are listed in Table I as a function of the initial CO vibrational quantum state \( v \). In the RRKM theory and the nonstatistical modification, the rate constant first decreases by about factors of 1.5 and 3, respectively, on going from \( v=0 \) to \( v=1 \) and then increases with further increase in \( v \). It is seen that \( v \) state-selected experiments, particularly \( v=0 \) and 1, would be helpful in clarifying the importance of nonstatistical effects in the reaction.

<table>
<thead>
<tr>
<th>( v )</th>
<th>RRKM</th>
<th>Nonstatistical</th>
<th>( K_{\text{non}}/K_{\text{RRKM}} )</th>
<th>Expt. (Ref. 32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.49</td>
<td>1.53</td>
<td>1.03</td>
<td>...</td>
</tr>
<tr>
<td>1</td>
<td>0.97</td>
<td>0.54</td>
<td>0.56</td>
<td>...</td>
</tr>
<tr>
<td>2</td>
<td>1.50</td>
<td>0.96</td>
<td>0.64</td>
<td>...</td>
</tr>
<tr>
<td>3</td>
<td>2.16</td>
<td>1.21</td>
<td>0.56</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>2.96</td>
<td>1.48</td>
<td>0.50</td>
<td>...</td>
</tr>
<tr>
<td>5</td>
<td>3.87</td>
<td>1.95</td>
<td>0.50</td>
<td>...</td>
</tr>
</tbody>
</table>

where \( v_{\text{min}}(T) = 298 \text{ K} \) and \( v_{\text{min}}(T) = 1400 \text{ K} \) and \( v_{\text{min}}(T) = 1800 \text{ K} \) are the same as indicated.

When \( v=1 \), \( N_1(J) \) is about equal to

\[
N_1(J) = N_1^0(J) = \int_{E_{\text{min}}}^{E_{\text{max}}-\hbar \nu} \rho^0(EJ) \kappa_2^0(EJ) \, dE',
\]

where \( E_{\text{min}} \) is about equal to 500 cm\(^{-1}\) lower and upper bounds of \( E \) are as indicated. \( E_0 \) is the potential energy plus the zero-point energy in HOCO'. The upper and lower bounds of \( E \) in Eq. (10) limit the amount of energy \( \xi \) transferring between other modes and the OH-stretching motion in TS2. When \( \xi \) approaches infinity, the energy transfer between modes is much faster than the lifetime of intermediates and the number of states used in the conventional RRKM is obtained at any \( n \), i.e., \( N_2^0(EJ) = N(J) \).

Using Eq. (9) and the rate constants \( k_2^0(EJ) \) for the reaction from the intermediate HOCO' with \( n \) quanta in the OH-stretching mode, the conventional RRKM rate constant at specified \( E \) and \( J \) can be expanded as

\[
k(EJ) = \frac{N(J)}{\hbar \rho(EJ)} = \frac{1}{n_{\text{max}}+1} \sum_{n=0}^{n_{\text{max}}} \rho^0(EJ) \kappa_2^n(EJ),
\]

since \( \kappa_2(E') = \kappa_2^0(EJ)/\hbar \rho^0(EJ), \) where \( \rho^0(EJ) \) is the density of states of the HOCO' at OH vibrational state \( n \). Equation (11) is Eq. (C3) (Ref. 42) in Ref. 28. The rate constant with nonstatistical modification can be obtained by using Eqs. (10) and (11) with a finite value of \( \xi \).

**FIG. 2.** Schematic profile of the relation between the HOCO' with total energy \( E \) including \( n \) quanta in the OH stretching and the OH energy interval \( nh\nu \xi \), permitting the entrance into TS2 in the nonstatistical model.

**FIG. 3.** The sums of states \( N_1(J), N_1^0(J), \) and \( N_1^{\text{non}}(J) \) are plotted vs \( E \). The chosen \( J \) state shown on this plot is the most probable \( J \) at room temperature. The plots of \( N_1^0(J) \) and of \( N_1(J) \) overlap in the energy range at current interest. The vibrational energy of CO at \( v=1,2 \) is indicated in the abscissa. In \( N_1^{\text{non}}(J) \) the bump around 3600 cm\(^{-1}\) is due to the increase of accessible OH-vibrational states in \( N_1^{\text{non}}(J) \).
$N_{v}^{\text{stat}}(E-h\nu)$, as seen in Fig. 4(a), but $N_{1}(EJ)$ and $N_{2}(EJ)$ are enhanced significantly over their values at $E-h\nu$. The increase in $N_{1}(EJ)$ is larger than that in $N_{2}(EJ)$, as seen in Fig. 3, because much of the energy in TS$_{2}$ goes into overcoming the need for tunneling rather than only in increasing the number of quantum states. Thereby, the key quantity in Eq. (5), $N_{v}^{\text{stat}}(EJ)/[N_{1}+N_{2}]$, decreases when $v$ is increased from 0 to 1, as seen in Fig. 4(b). At higher $v$, and hence higher energies, $N_{2}(EJ)$ increases with $E$ more rapidly than does $N_{1}(EJ)$ (Fig. 5), perhaps because $T_{S_{1}}$ has more rotations (hindered) than $T_{S_{2}}$, and the number of quantum states increases less rapidly for rotations (one squared term per coordinate) than for vibrations (two squared terms per coordinate). Thus, for $v=1,2,\ldots$, the ratio $N_{2}(EJ)/[N_{1}(EJ)+N_{2}(EJ)]$ increases with energy (Fig. 5), and so the rate constants also increase with increasing $v$.

The present calculated result for $v=1$ compared with $v=0$ is different from the classical trajectory results of Lakin et al., but the trend from $v=1$ to $v=2$ is in the same direction: Their calculation showed a cross section for the reaction that increased monotonically when $v$ was increased from 0 to 2. The difference may have several origins, one being the absence of the quantum-mechanical tunneling in the exit channel transition state when classical trajectories are used. The consequences of this tunneling effect produce the decrease in $k^{0}$ on going from $v=0$ to $v=1$.

Because of the limited amount of internal energy transfer in the exit channel in the nonstatistical model [Eqs. (9) and (10)], the energy dependence of $N_{v}^{\text{stat}}(EJ)$ is smaller than that of $N_{2}(EJ)$ of the RRKM theory. Thereby, the nonstatistical model has a weaker energy dependence of $[N_{1}(EJ)+N_{2}^{\text{stat}}]$ on $v$, and so the enhancement of $N_{v}^{\text{stat}}(EJ)$ noted above with increase in $v$ is less than that of $N_{2}(EJ)$, as seen in Fig. 3, and so the decrease in the $k^{0}$ value from $v=0$ to $v=1$ is larger.

Since the calculated $k^{v=2}$ value is smaller than $k^{v=1}$, the rate constants at higher vibrational temperatures are lower than the value at room temperature for the vibrational temperatures studied, 298, 1400, and 1800 K, as seen in Fig. 6. In the experiment the rate constant in this range of $T_{v}$'s is smaller than the room-temperature value by 10% at 1400 K and 15% at 1800 K (but with large error bars). The calculated rate constants at the two temperatures, $k_{\text{total}}(T_{v}=1400)$ and $k_{\text{total}}(T_{v}=1800)$, are lower than $k_{\text{total}}(T_{v}=298)$ by 7% and 12%, respectively, in the modified statistical theory and by 3% and 5% in the unmodified RRKM theory. The trend is seen in Fig. 6.

We also note that quantum-mechanical calculations or perhaps classical trajectories can test the validity of the simple nonstatistical model assumed in Fig. 2. In passing we also note one property seen in Fig. 3 not needed in the discussion of the effect of $v$ at room temperature but of interest at low temperature: At energies below $\sim 300$ cm$^{-1}$ we have $N_{1} < N_{2}$. Its origin is that although the barrier at TS$_{2}$ is somewhat higher than at TS$_{1}$ there is so much tunneling at TS$_{2}$ that the bottleneck at these low energies now occurs at TS$_{1}$, i.e., $N_{1} < N_{2}$. 

FIG. 4. The sums of states $N_{v}(EJ)$ and $[N_{1}(EJ)+N_{2}^{\text{stat}}(EJ)+N_{v}^{\text{stat}}(EJ)]$ obtained with the nonstatistical theory are plotted vs $E$, total energy $E$ minus $v\hbar\nu$ at the specified $v$. The solid black, dotted black, and the solid gray lines denote the plots for $v=0,1,$ and 2, respectively. The chosen $J$ state shown on this plot is the most probable $J$ at room temperature.

FIG. 5. Sums of states $N_{v}(EJ)$ and $[N_{1}(EJ)+N_{2}^{\text{stat}}(EJ)+N_{v}^{\text{stat}}(EJ)]$ plotted vs $E$ at typical $J$. In nonstatistical calculations $N_{v}^{\text{stat}}(EJ)$ is used instead of $N_{v}(EJ)$. The difference is the value obtained with the nonstatistical modification minus that with the RRKM theory. The vibrational energy of CO at $v=1,2$ is indicated in the abscissa. In the nonstatistical calculations and the difference, the small bump around 3600 cm$^{-1}$ is due to the increase of accessible OH-vibrational states in $N_{v}^{\text{stat}}(EJ)$.
FIG. 6. Plot of rate constants vs CO-vibrational temperature $T_v$. The temperature for the other coordinates is 298 K. The calculated rate constants obtained with the RRKM theory and with the nonstatistical modification are shown by the gray and black lines, respectively. The open triangles and error bars are taken from the experimental data of Dreier and Wolfrum (Ref. 32).

IV. CONCLUSIONS

Both the RRKM and the nonstatistical modified theory yield a decrease in rate constant for the OH+CO $\rightarrow$ H+CO$_2$ reaction at higher CO-vibrational temperatures. Because of the limited energy transfer rate in the nonstatistically modified theory, the effect is stronger in the modified theory than in the standard RRKM theory and is also closer to the apparent experimental results. State-selected experiments as a function of $v$ are predicted (Table I) to first decrease and then increase with increasing $v$ and, of course, yield much larger effects than vibrationally averaged results.

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