A New OH Vibrational Distribution Model Developed Using Molecular Dynamics

Deborah A. Levin and Sergey F. Gimelshein

George Washington University, Washington, DC 20052

Abstract. A semi-classical molecular dynamics approach is used to model the dissociation of water to form the hydroxyl radical. The unimolecular dissociation of water is used to calculate the probability of reaction as well as determine the product OH translational, vibrational, and rotational energy distributions. The molecular dynamics probabilities of reactions and product distributions are used in the direct simulation Monte Carlo method to model spatial distribution and temperatures of OH in the bow-shock of a 5 km/sec vehicle at 80 and 100 km. Ultraviolet spectra of the OH($X \rightarrow A$) transition are computed and compared with data from the Bow Shock Ultraviolet Flight Experiment 2. Excellent agreement of the spectral features between theory and experiment is obtained.

INTRODUCTION

Ultraviolet radiation from the OH ($A \rightarrow X$) system has been studied extensively in the combustion and atmospheric sciences communities. [1] The hydroxyl radical is readily observed under various hypersonic flow conditions where it is produced by shock chemistry reactions. [2] The strong spin-allowed transition from the first excited state, $A^2\Sigma^+$, to the ground state means that it is easily observable, even when present in trace quantities. A quality spectrum of OH was taken at an altitude of 100 km during the Bow Shock Ultraviolet Flight Experiment 2 (BSUV2). The mission and spectrometer instrumentation have been described in detail in earlier work. [3] The 1 nm spectral data capture an environment difficult or impossible to duplicate in ground facilities. Earlier work demonstrated the sensitivity of the spectra to variation in the vibrational temperature. [4] The data show that the OH vibrational temperature could be as high as 7,000 K or as low as 4,000 K depending upon which spectral features are given more emphasis. Nevertheless, the OH vibrational temperature is significantly different than the predicted shocklayer bulk ($N_2$) vibrational temperature of $\sim 2,000$ K as is possible with the radiation being produced in a rarefied flow.

To date, there has been no fundamental explanation of why the OH vibrational temperature in such flows is different from that of $N_2$. More detailed treatment of the coupling of the flow and radiation modeling has been undertaken for the OH($A$) system. [5] This work, however, does not lead to OH vibrational temperatures consistent with the BSUV 2. We have shown in earlier work [6] that the OH is formed by the dissociation of water through collisions with, primarily, $N_2$. Hence if we are to understand the formation of vibrationally hot OH, we must expect to model in detail the dissociation of water. The goal of this work is to present calculations of recently obtained vibrational distributions of OH formed by water dissociation. The nascent OH vibrational and rotational state distributions have been calculated from the semi-classical molecular dynamics trajectory method. The degree to which the nascent distributions will be sustained in the flow depends on the collision rate. The flow conditions corresponding to BSUV2 are transitional and can only be represented by a rarefied gas technique. Hence the direct simulation Monte Carlo (DSMC) method will be used.

---

1) The work was supported by the Army Research Office Grant DAAG55-98-1-009 and the Ballistic Missile Defense Organization and AFOSR Grant F49620-99-1-0143.
Molecular dynamics enables one to calculate from first principles probabilities, cross sections, and rate constants for fundamental elementary reaction processes. Since these quantities depend on the motion of the atomic nuclei, a classical rather than (exact) quantum treatment of that motion has been shown to provide a good approximation for the investigation of reaction mechanisms. [7] The potential energy surface (PES) represents the change in electronic energy as a function of the internuclear distances. When the potential energy surface is obtained using fits to a series of quantum mechanical single energy point calculations, the scattering method is referred to as a semi-classical one. For tritatomic molecules, reliable surfaces have been generated using ab initio quantum mechanical calculations as well as experimental data. [8] Such surfaces do not exist unfortunately for the H\textsubscript{2}O - N\textsubscript{2} interaction. For the collision energies of interest (~1.7 eV), the neutral colliders (N\textsubscript{2}, O\textsubscript{2}, or O) dissociate water primarily by transferring their kinetic energy to the vibrational modes of water. A classical trajectory calculation of unimolecular water dissociation (i.e., water self-dissociation) using an accurate water PES can approximate the resultant OH vibrational and rotational product distribution.

The classical Hamiltonian for the water molecule may be expressed as

\[ H = T + V = E \]  

where \( T \) is the sum of kinetic energies of all three water nuclei and \( V \) is the potential energy of water (a function of the three water internuclear distances). For systems of three nuclei and larger, it is most convenient to express the Hamiltonian in the laboratory reference frame in a Cartesian coordinate system. For three nuclei, Hamilton’s equations of motion become,

\[ \ddot{r}_{ij} = \frac{\partial V}{\partial r_{ij}}, \quad \dot{p}_{ij} = \frac{p_{ij}}{m_i} \]  

where the dotted symbol denotes a time derivative, \( i = 1,2,3 \) (atoms), \( j = 1,2,3 \) (dimensions); \( p_{ij} \) and \( r_{ij} \) are the Cartesian momenta and coordinates for the \( i \)-th atom in the \( j \)-th direction, and \( m_i \) is the mass of the \( i \)-th atom. The eighteen coupled equations can be solved for the coordinates and momenta of the three atom system using a fourth-order Runge-Kutta method. [9] The two valued surface-ground state PES for water calculated by Murrell et al [10] was used in this work. The use of two diabatic surfaces gives the an accurate ground state water PES in the dissociation region, the prime region of interest in our calculations.

Considerable studies have been carried out for the unimolecular dissociation of water. [11-13] These studies, however, have emphasized the product distribution for considerably higher dissociation energies (~ 9.5 eV) and from the electronically excited states of water and the product distribution of the OH(A) state. Since the energetics of the BSUV2 flows are clearly not this high, the results of earlier unimolecular dissociation studies are not applicable. Moreover, the BSUV 2 data suggest that the OH(A) state is populated after OH(X) has been formed. [6] Hence detailed OH(X) product distributions are needed for the energy range of present interest to be used in the DSMC method.

The use of the molecular dynamics unimolecular dissociation to predict a probability of dissociation in the DSMC simulation requires that a specific time constant for water dissociation be chosen. Calculation of the probability of the dissociation of water by a collider would avoid this question because the length of the interaction time would be determined in the context of the scattering calculation and would be a function of the relative collisional velocity and the interaction potential. An approximation to the probability can be made by assuming that the interaction time corresponding to the specific time constant is the ratio of obtained by DSMC variable hard-sphere diameters of water and the collider (N\textsubscript{2}) to their relative velocity. It is worthwhile to test this approximation because potential surfaces for larger target molecules and their colliders are generally not available.

Figure 1 shows a comparison of the dissociation rate given by the total collisional energy (TCE) [14] and unimolecular dissociation models. Two extreme conditions are shown for the TCE rate, those where all precollisional energy modes are included versus the case when only the pre-collisional translational energy is included. The energy dependence of the unimolecular rates at various interaction times are also shown. The unimolecular probabilities are seen to have a different energy dependence than the two cases of the TCE model. Moreover, the unimolecular probabilities approach unity as the energy is increased, whereas the TCE model, which is most often used in DSMC calculations, does not.
The use of the unimolecular dissociation to predict dissociated product state distributions is the second, and perhaps more important, result of the molecular dynamics approach. For each trajectory, the water is determined to have dissociated if the distance between the H atom and the OH molecule is sufficiently great (larger than 5Å). The energy after the dissociation is divided into the following components,

\[ E = E_{cm}^T + E_{H,OH}^{Tr} + E_{OH}^{Tr} + V_{OH} = E_{cm}^R + E_{H,OH}^{Tr} + E_{OH}^{int} \]  

where the last term represents the internal energy of OH. The rotational and vibrational energies of the OH molecule can be described classically and vibrational and rotation motion are assumed to be separable. [15]

The quantum mechanical vibrational energy is related to the classical radial motion through the radial action variable, \( \nu \).

\[ \nu = \frac{1}{2} + \frac{2\mu}{\hbar} \int_{R_>}^{R_<} \dot{R}dR \]  

The OH radial motion is analyzed to determine the turning points, \( R_> \) and \( R_< \), and to obtain \( \nu \) the integral is performed numerically over half a vibrational cycle. The variable \( \nu \) then corresponds to the usual quantum mechanical vibrational quantum number.

Figure 2 shows the OH product vibrational number distributions obtained from the molecular dynamics trajectory calculations. These product distributions (as well as the rotational and relative translational energy) are used as a data base in the DSMC flow modeling. This figure shows the change in vibrational distributions for different water internal energy values. At internal energies below 50,000 cm\(^{-1}\) there is insufficient energy to populate the \( \nu = 1 \) vibrational level whereas at 70,000 cm\(^{-1}\) the higher levels (up to seventh) are significantly populated. Also as the energy is raised the effective vibrational temperature increases and the vibrational populations follow a Boltzmann distribution. A variation in rotational distributions for different vibrational levels and water energies was also obtained. Except for the lowest internal energy, it was found that the rotational populations deviate strongly from a Boltzmann distribution.

NUMERICAL METHOD

The SMILE computational tool [16] based on the DSMC method will be used in computations. The majorant frequency scheme is employed for modeling molecular collisions. [17] The variable hard sphere model was used for modeling intermolecular interactions. The Larsen-Borgnakke model [18] with temperature-dependent rotational and vibrational relaxation numbers was utilized for rotation-translation and vibration-translation energy transfer. The TCE model was employed to calculate all gas-phase chemical reactions involving the chemical species N\(_2\), O\(_2\) and their derivatives. The complete list of N\(_2\), O\(_2\) reactions may be found in earlier work [19] and the additional hydrogenated reactions used in this work are given in Table 1. The OH and H\(_2\)O species were considered as trace species whose weighting factor was varied from 10\(^{-9}\) to 10\(^{-5}\) depending on the altitude considered. The number of simulated molecules in the computational domain was about 1,300,000, which is quite sufficient to avoid any influence of statistical dependence on the modeling results. Different adaptive to flow gradients grids were used to model collisions and macroparameters. The total number of collision and macroparameter cells was about 150,000 and 30,000, respectively.

The results will be compared for altitudes 80 and 100 km using three reaction probability/energy redistribution models for the water dissociation reactions (the first three reactions of Table 1). The baseline model (TCE-HM) is the TCE model with the energy redistribution (HM) similar to that presented by Haas [20]. The algorithm for the redistribution is as follows. First, the total collision energy \( E_c \) is calculated. Then, all energies (relative translational, rotational, and vibrational) are multiplied by a factor of \( (E_c - E_d)/E_c \), where \( E_d \) is the water dissociation threshold. The new velocities of H\(_2\)O and a collision partner are calculated. Afterwards, the H\(_2\)O molecule is divided into OH and H. The energies of the OH–H pair (relative translational and OH internal energies) are calculated so that the magnitude is proportional to the number of degrees of freedom of the corresponding modes, and the sum is equal to the sum of rotational and vibrational energies of H\(_2\)O. Finally, new velocities of OH and H are calculated using new relative translational energy of OH–H pair and the velocity of the center of mass equal to the H\(_2\)O velocity. With such a redistribution, the internal energies of OH are proportional to the internal energy of H\(_2\)O. Where relevant, results will be shown for water dissociation probabilities obtained from the unimolecular dissociation calculations with HM redistribution.
TABLE 1. Rate Coefficients for Hydrogenated Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient, m³molec⁻¹s⁻¹</th>
<th>$A$</th>
<th>$n$</th>
<th>$E/k_B$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} + \text{N}_2 \rightarrow \text{OH} + \text{H} + \text{N}_2$</td>
<td>$5.81 \times 10^{-15}$</td>
<td>0.000</td>
<td>-53,000.0</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{OH} + \text{H} + \text{O}_2$</td>
<td>$1.13 \times 10^{-7}$</td>
<td>-1.31</td>
<td>-59,400.0</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{H} + \text{O}$</td>
<td>$1.13 \times 10^{-7}$</td>
<td>-1.31</td>
<td>-59,400.0</td>
<td></td>
</tr>
<tr>
<td>$\text{OH} + \text{N}_2 \rightarrow \text{O} + \text{H} + \text{N}_2$</td>
<td>$1.25 \times 10^{-15}$</td>
<td>0.06</td>
<td>-51,000.0</td>
<td></td>
</tr>
<tr>
<td>$\text{OH} + \text{O}_2 \rightarrow \text{OH} + \text{H} + \text{O}_2$</td>
<td>$1.25 \times 10^{-15}$</td>
<td>0.06</td>
<td>-51,000.0</td>
<td></td>
</tr>
<tr>
<td>$\text{OH} + \text{O} \rightarrow \text{OH} + \text{H} + \text{O}$</td>
<td>$1.25 \times 10^{-15}$</td>
<td>0.06</td>
<td>-51,000.0</td>
<td></td>
</tr>
<tr>
<td>$\text{H} + \text{O}_2 \leftrightarrow \text{OH} + \text{O}$</td>
<td>$3.65 \times 10^{-16}$</td>
<td>0.00</td>
<td>-8,450.0</td>
<td></td>
</tr>
<tr>
<td>$\text{O} + \text{H}_2\text{O} \leftrightarrow \text{OH} + \text{OH}$</td>
<td>$1.13 \times 10^{-16}$</td>
<td>0.00</td>
<td>-9,240.0</td>
<td></td>
</tr>
</tbody>
</table>

(UD-HM model). Finally, the third model utilizes the unimolecular probabilities with the unimolecular OH product distribution results (UD-MD model). The details of the energy redistributions are given above. Note here that the OH energy distribution depends on the sum of relative translational energy of reagents and H₂O internal energy.

In earlier work [4] we discussed the requirement and development of a spectroscopic/collisional radiative model for modeling the OH($A^2\Sigma^+ \rightarrow X^2\Pi$) spectra in hypersonic flows. The model developed consists of two parts, the excitation and spectroscopic portions. The excitation portion of the model incorporates statespecific processes, including quenching, predissociation, radiation, and vibrational-rotational exchange. The spectroscopic portion includes the most accurate OH line positions and transition probabilities.

Using the steady state DSMC flow solution which provides a two-dimensional spatial distribution of species concentrations and temperatures, the radiation can be calculated. Modification so the NEQAIR model [4] for OH, an accurate line-by-line spectroscopic model with radiative transport, was used. The OH($A$) vibrational and rotational state distributions were obtained from the full quasi-steady state model given in earlier work [4] using the flowfield ground state OH concentrations and rotational and vibrational temperatures calculated in the present work. It will be shown that the OH vibrational and rotational populations obtained from the molecular dynamics redistribution method follow a Boltzmann distribution. Hence the use of vibrational and rotational temperatures, instead of populations, is not significant. Spectra were simulated using a spectral resolution of 0.0056 Å and averaged over a 10 Å triangular line shape which approximates the Erdman-spectrometer flown on BSUV2. [21]

**COMPUTATIONAL RESULTS**

Let us first discuss the macroscopic parameters of the flow calculated using the baseline chemistry model, TCE-HM. For parameters dominated by the bulk flow species, N₂, O₂, and O, the distributions will be determined by the TCE-HM model. Table 2 gives the free stream conditions for the two altitudes for which results will be shown. Figure 3 shows the distributions of the total number densities for 80 and 100 km using the baseline chemistry model. The difference in distributions illustrates the growth of the shocklayer as the rarefaction increases. The difference in the bulk translational, rotational, and vibrational temperatures for the two extreme altitude conditions can be seen in closer detail by examining the spatial distribution along the stagnation streamline. Figure 4 shows the flow exhibits thermal nonequilibrium. Even stronger thermal nonequilibrium is observed for higher altitudes. Note, all temperatures are lower for higher altitudes. The reduction in the bulk translational temperature, as well as number density, at higher altitudes indicates that the water dissociation rate will be reduced for all of the three chemical models considered here.

Consider now the sensitivity of the OH concentrations and temperatures to the three water dissociation chemistry models. First, let us examine the sensitivity of OH production to the water dissociation model, i.e., TCE-HM and UD-HM. Figure 5 shows the change in OH number density at 80 km for these two models. At 80 km the shape of OH profiles are very similar for both chemistry models, with the TCE model larger by approximately a factor of two. The difference between the two models is approximately the same for higher
FIGURE 1. Comparison of the probability of dissociation as a function of relative collisional energy for the TCE and unimolecular dissociation.

FIGURE 2. Comparison of OH vibrational distributions at different water energies.

FIGURE 3. Comparison of total number densities normalized by free-stream values for 80 km (top) and 100 km (bottom) calculated using the baseline, TCE-HM model. Axes are in m.

FIGURE 4. N₂ temperature profiles along the stagnation streamline for 80 km calculated using the baseline, TCE-HM model.

FIGURE 5. Comparison of OH number density profiles along the stagnation streamline at 80 km for the TCE-HM and UD-HM models. The body is located at X = 0.

FIGURE 6. Comparison of OH temperature profiles along the stagnation streamline at 80 km for different methods of energy redistribution (UD-HM vs UD-MD) models. The body is located at X = 0.
TABLE 2. Free Stream Conditions

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>Total Number density number/m$^3$</th>
<th>water mole fraction</th>
<th>OH mole fraction</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>$4.18 \times 10^{20}$</td>
<td>$5.6 \times 10^{-6}$</td>
<td>$4.3 \times 10^{-9}$</td>
<td>181</td>
</tr>
<tr>
<td>100</td>
<td>$1.19 \times 10^{19}$</td>
<td>$7.2 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-10}$</td>
<td>185</td>
</tr>
</tbody>
</table>

altitudes. The success of the unimolecular dissociation method to predict water dissociation probabilities instead of a full scattering calculation is important in terms of an accurate modeling of dissociative collisions between large polyatomic systems where a full scattering calculation may not be practical.

The second comparison that we consider is that of OH temperatures. The OH temperature distributions are dependent on the manner of product energy redistribution and hence comparisons are shown for the UD-HM and UD-MD models. (It was found that the OH temperatures obtained from the baseline model were identical to that of the UD-HM model.) The OH temperature profiles obtained by these two water chemistry models were found to be considerably different. Figure 6 shows a comparison of the OH translational, rotational, and vibrational temperatures along the stagnation streamline at 80 km for the two different models of energy redistribution. It can be seen that the OH translational temperature profile is identical for either model, but the OH rotational and vibrational temperatures have a different spatial distribution. In the region where the rotational temperature reaches a maximum, both models give similar results, and in the shock front the HM method underpredicts the MD temperatures. The OH vibrational temperatures, however, are both substantially different in terms of magnitudes and shapes. Figure 7 shows the same results at 100 km. Similar to the 80 km predictions, only the OH translational temperature profiles are the same for both methods of energy redistribution. The number of collisions in the flow is sufficiently small at 100 km, that both the rotational and vibrational temperatures obtained by the HM energy redistribution procedure are found to be significantly lower than those obtained with the molecular dynamics.

The OH temperature profiles shown in Figs. 6 and 7 are derived assuming a vibrational equilibrium distribution at each location in the flow. To understand these spatial profiles it is useful to examine the vibrational distribution functions at a region in the flow where the radiation will be a maximum (along the stagnation streamline and close to the body). Figure 8 provides a comparison of these distributions for the HM and MD energy redistribution methods at 80 km. For the same flow conditions the MD vibrational populations are higher than that obtained with the HM method, and only the MD populations follow a Boltzmann distribution. The reason for that is that in the HM technique the vibrational energy of OH is proportional to the internal energy of H$_2$O multiplied by $(E_c - E_d)/E_c$. In turn, the H$_2$O internal energy is strongly nonequilibrium. Figure 9 shows the H$_2$O internal energy distributions at three different locations along the stagnation line, $X = -0.03$ (the shallow portion of the shock wave), $X = -0.01$ (the region where the translational temperature is a maximum), and $X = -0.002$ (the vicinity of the surface). The degree of nonequilibrium is explained by the presence of internally cold free stream molecules whose concentration is significant even at the location close to the wall. The MD distribution is close to equilibrium since it principally depends on relative translational energy that is almost equilibrium. Figure 10 presents a similar comparison of the vibrational distributions at an altitude of 100 km. As the flow rarefaction increases the differences in the vibrational state distributions also increases. Note that the vibrational states obtained from the MD continue to follow a Boltzmann distribution.

In previous work [4] we showed that the BSUV2 high altitude OH spectra could only be modeled if one assigned vibrational and rotational temperatures that were considerably different from that of the bulk flow. This conclusion is possible because the OH ultraviolet spectral shape is sensitive to both its vibrational and rotational temperature. The ratio of the peak heights at 2800 Å (the 1-0 band) and the 3100 Å (the 0-0 band) and the shape of the right shoulder of the 3100 Å peak depend mainly on the vibrational temperature. The relative intensity of the two peaks of the 0-0 band between 3060 and 3100 Å is a function of the rotational temperature only. Unimolecular dissociation calculations by Nyman et al [12] showed that the OH product vibrational and rotational temperatures were non-Boltzmann, but did not provide the data required for a quantitative flow and spectral calculation. Using the OH temperatures obtained in this work and the generalized spectroscopic model of previous work [4] we predict the OH ultraviolet spectra in a fully consistent manner and compare our results with the BSUV2 data.

Figure 11 shows a comparison of the predicted spectra at 80 km along the stagnation streamline computed
**FIGURE 7.** Comparison of OH temperature profiles along the stagnation streamline at 100 km for different methods of energy redistribution (UD-HM vs UD-MD) models. The body is located at $X = 0$.

**FIGURE 8.** Comparison of OH vibrational distributions at 80 km for different methods of energy redistribution (UD-HM vs UD-MD) models. $X = -0.009$ m, $Y = 0$.

**FIGURE 9.** Comparison of H$_2$O internal energy distributions at 80 km at three different locations along the stagnation line.

**FIGURE 10.** Comparison of OH vibrational distributions at 100 km for different methods of energy redistribution (UD-HM vs UD-MD) models. $X = -0.1$ m, $Y = 0$.

**FIGURE 11.** Comparison of OH ultraviolet spectra at 80 km computed using the TCE-HM and UD-MD water dissociation models.

**FIGURE 12.** Comparison of OH ultraviolet spectra at 100 km computed using the TCE-HM and UD-MD water dissociation models and comparison with the BSUV2 data.
using the TCE-HM and the UD-MD water dissociation models. The salient differences are seen in the ratios of the (0-0) to (1-0) peaks as well as the width of the (0-0) peak. Both features are strongly dependent on the OH vibrational temperature. Finally, Fig. 12 shows the comparison at 100 km altitude of the spectra predicted by the TCE-HM and the UD-MD models with the BSUV2 data. It can be seen that the spectra computed with the UD-MD water dissociation model is in much better agreement with the data. The spectra generated with the TCE-HM model does not predict any (0-1) vibrational peak contribution. The minor disagreement between the data and the UD-MD models indicates that the latter may predict OH vibrational and rotational temperatures that are slightly too high.

CONCLUSIONS

A semi-classical molecular dynamics approach has been used to model the dissociation of water to form the hydroxyl radical. The unimolecular dissociation of water is used to model the probability of reaction as well as determine the product OH translational, vibrational, and rotational energy distributions. These data have been incorporated into the DSMC method to predict flow OH concentrations and state distributions. Using a generalized OH collisional/radiative model with the DSMC flow simulations, spectra from the OH(X → A) ultraviolet transition have been modeled. Comparison of simulated spectra with experimental data show that the predicted spectra agree well at all altitudes. Thus we offer the first fundamental explanation of why the OH vibrational and rotational temperatures are different from the bulk values.

Specifically, we note that the unimolecular dynamics water dissociation rates are similar to those predicted by the TCE model for this reaction. However, when we compare the product distributions obtained from the trajectory calculations with those derived from the local equilibrium model we find that the distributions are significantly different. The molecular dynamics predicts a greater relative population of the higher OH vibrational states and in fact the vibrational states follow a Boltzmann distribution. As the flow rarefaction increases, the differences between the two redistribution techniques becomes more important.

REFERENCES