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13. ABSTRACT *(Maxiumum 200 words)*

We are developing improved models for low-density, high temperature flows of reacting air, and using these models to study recent re-entry flight experiment data. We have used computational chemistry methods to obtain the first accurate data for the primary nitric oxide formation reaction under thermal conditions. We have also carefully studied the internal energy state of the nitric oxide formed by this reaction. This model will be implemented in continuum and particle flow field solution methods during the next year. We have also developed a new dissociation modeling approach for particle simulation methods; this approach gives significantly higher levels of dissociation under strongly nonequilibrium conditions. These new models will greatly enhance our ability to predict the radiative emission from re-entry flows.

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SIMULATION OF NONEQUILIBRIUM AEROTHERMOCHEMISTRY USING CONTINUUM AND PARTICLE METHODS

FINAL REPORT

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April 20, 2000

U. S. ARMY RESEARCH OFFICE

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STATEMENT OF THE PROBLEM STUDIED

Continuum and particle simulation methods were used to study the radiative emission from high Mach number shock layers at high altitudes. The focus of the effort was on the accurate physical modeling of the fluid motion and its interaction with the chemical reactions. Particular emphasis was given to the modeling of the Zeldovich reactions that form the most important radiator, which is the nitric oxide molecule. The approach involved using state-of-the-art continuum computational fluid dynamics (CFD) methods and the direct simulation Monte Carlo (DSMC) method that is designed for rarefied flows. The combination of these two methods was powerful and allowed us to investigate and improve the weaknesses of the two methods. In addition, extensive computational chemistry calculations were performed to determine the high-temperature characteristics of the Zeldovich reactions. This work was used to develop a new advanced thermo-chemical model for nitric oxide, and this model resulted in much more accurate predictions of the radiation emitted from high Mach number shock layers.

SUMMARY OF MOST IMPORTANT RESULTS

The project resulted in a number of key findings which are summarized here. The research focussed on the analysis of the experimental data from two small rocket flight experiments, Bow Shock Ultraviolet-1 and -2. BSUV-1 flew at about 3.5 km/s at altitudes from 40 km and above. BSUV-2 flew at a higher speed of 5.1 km/s and from altitudes of about 100 km down to about 70 km. Further information may be obtained from the technical papers that resulted from this work.

Prior to the current research, the prediction of the radiation from high-temperature shock layers was woefully inadequate. For example, Fig. 1 shows the pre-flight prediction of the radiation in the 230 nm spectral region, as compared to the flight data. We see that the predictions are reasonable at low altitudes, but at high altitudes the predictions are too low by more than a factor of 10^9 (one billion!). The research performed under this grant clarified the reasons for this difference, and resulted in models that can predict the radiation from these flow fields within the uncertainty of the atmospheric conditions at high altitude. This typically results in a factor of two uncertainty in the predicted radiative signal.

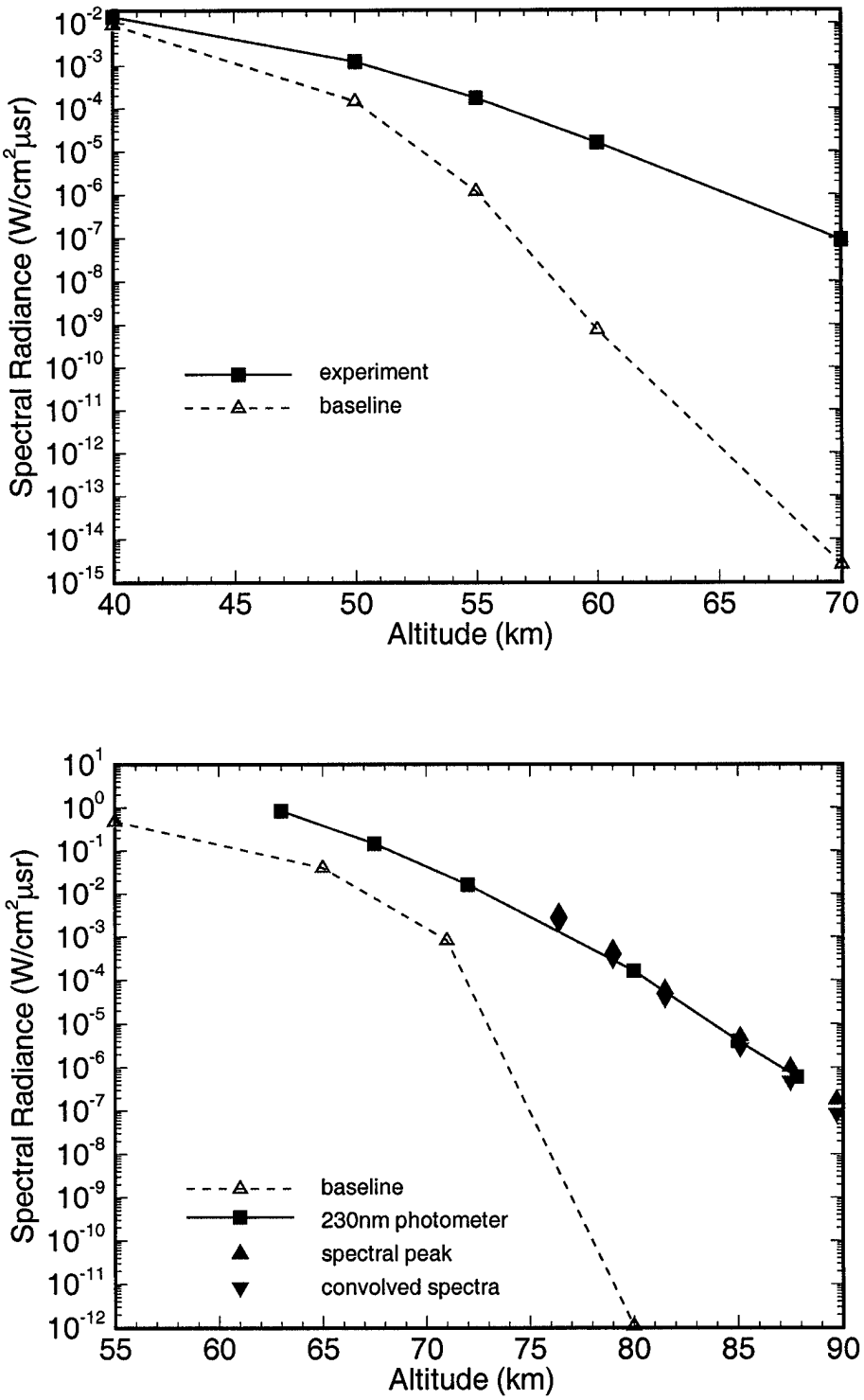

Figure 1. Pre-flight radiative emission predictions in the 230 nm spectral region for BSUV-1 (top) and BSUV-2 (bottom).

High Altitude Flow Simulations

The first part of the research involved careful comparisons between a conventional continuum flow simulation method and a particle-based flow simulation approach. This work showed that the two methods gave remarkably similar results except in certain regions of the flow. For example, consider Fig. 2, which plots the temperatures and nitric oxide number density along the stagnation streamline for the BSUV-2 flight conditions at a relatively high altitude of 88 km. We see that the continuum CFD method and the DSMC method agree with each other, except that there is a difference in the peak translational and rotational temperatures. Also the particle-based method predicts a thicker shock wave, as expected.

Based on the comparisons between the continuum and particle simulation approaches, we developed a new Navier-Stokes equations failure detection mechanism. This idea is based on work of Bird and others, but through careful comparison of various candidate criteria, we found that the gradient-length-local Knudsen number is the most accurate. In particular, for these flows with the parameter based on the local density gradient, the criterion

$$Kn_{\mathrm{GLL}} = \frac{\lambda}{\rho}\left|\frac{\partial \rho}{\partial \ell}\right| > 0.05$$

was found to be the most accurate to determine the locations of failure of the continuum formulation. That is, where $Kn_{\mathrm{GLL}} > 0.05$, the Navier-Stokes equations are expected to fail. (Note that the density gradient is taken in the direction of largest gradient in the above equation.)

Interestingly enough, it was also found that the DSMC formulation may also fail in the simulation of these flows. This can occur when trace chemical species are important. Because the DSMC method represents the flow with a much smaller number of particles than actually exists, there can be statistical sampling problems. In this case, a trace species that may be present in parts per million, for example, may never be formed by the DSMC formulation. These trace species may in fact be very important for the prediction of radiation from these flows. A new approach was developed to include trace species in the DSMC formulation by applying a trace-species weighting approach. This weighting was carefully formulated to assure mass, momentum, and energy conservation by the method. This allowed us to simulate flows with trace species efficiently.

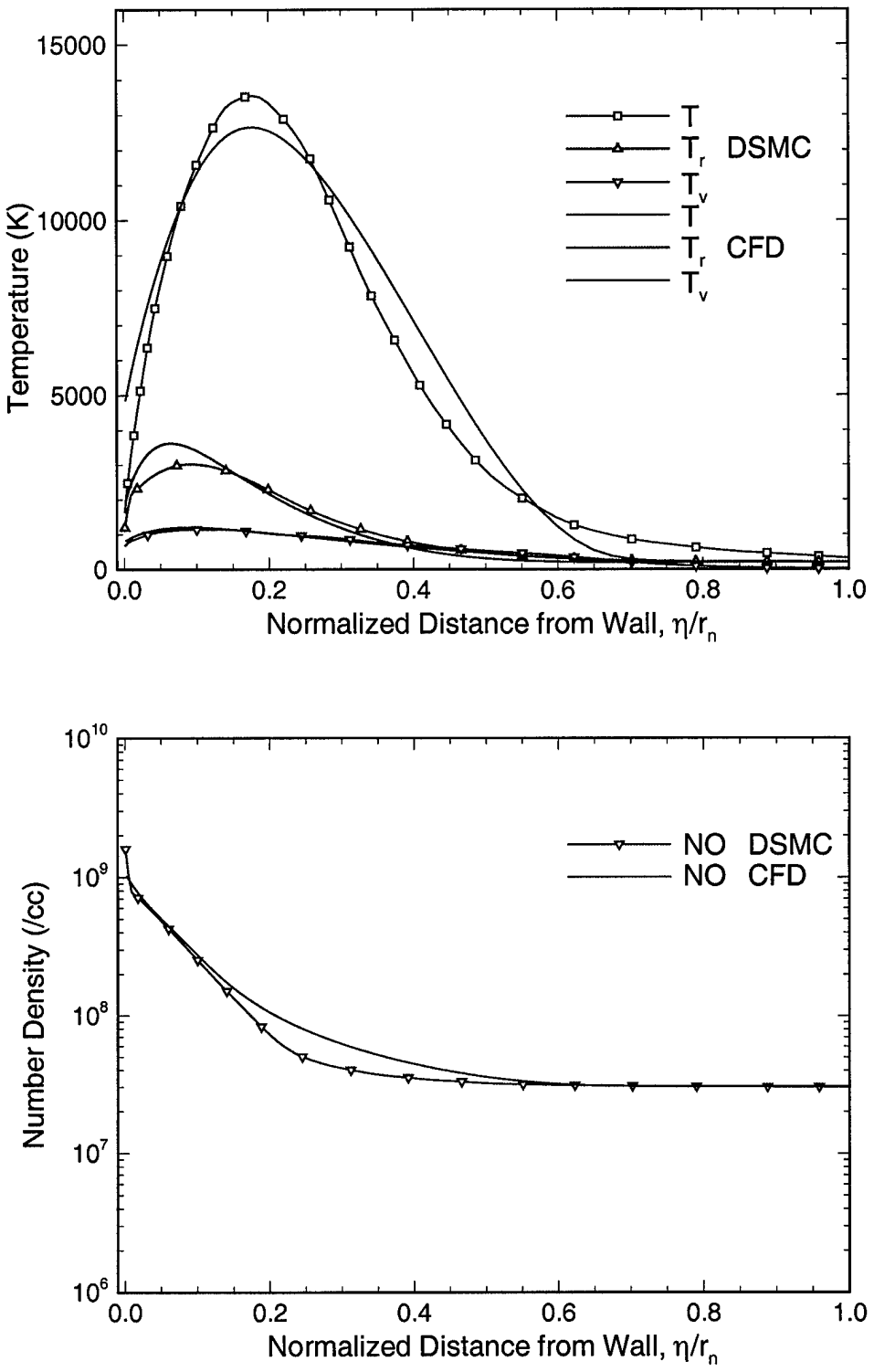

Figure 2. Computed stagnation streamline temperatures (top) and nitric oxide number density (bottom) for the BSUV-2 flight at 88 km.

Zeldovich Reaction Modeling

Almost all of the radiative signal from the flow field shown in Fig. 1 is from the nitric oxide molecule. Therefore, the predicted signal is very sensitive to the rate of formation of nitric oxide in these high-temperature, low-density flows. Nitric oxide is formed through the coupled Zeldovich reactions. First, small levels of oxygen dissociation occur that result in the formation of oxygen atoms, or at high altitude, significant levels of oxygen are present in the atmosphere. The O atoms then react to form nitric oxide (NO) through

$$N_2 + O \rightleftharpoons NO + N$$

then because the N atoms formed by this reaction are highly energetic, they may react by the second Zeldovich reaction to form more NO and O

$$O_2 + N \rightleftharpoons NO + O$$

The cycle can then repeat itself, resulting in additional production of nitric oxide.

Prior to the current research, these reactions had had considerable attention because they are the main mechanism for the production of thermal NO_x in combustion. However, the reaction rate data for these reactions was obtained at significantly lower temperatures than encountered during re-entry. (See Fig. 2.) More importantly, the reaction rates vary with the internal energy of the reacting particles, and since there is very significant thermal nonequilibrium in these flows, this must be considered in the computation of the reaction rates. In addition, the radiative signature depends on the internal energy distribution of the radiating molecule. Therefore, we found it necessary to understand how the internal energy of the nitric oxide molecules is distributed after they are formed. For example, when the second Zeldovich reaction produces NO ($O_2 + N \rightarrow NO + O$), there is excess energy due to the release of chemical energy. This energy is placed in the translation and vibrational energy of the products. Thus, NO may be formed with high vibrational temperature, which results in a significantly increased radiative signature.

Because of these issues, an extensive computational chemistry study was conducted to compute high-temperature reaction rates for the Zeldovich reactions. These rates were obtained as functions of the vibrational and rotational energies of the interacting particles. We also did careful accounting to determine how the energy was disposed to the internal energy modes after the reactions. This work produced a complete high-temperature reaction rate database to allow us to formulate a much more accurate and widely-applicable model for NO formation in re-entry shock layers.

Examples of the work are given in Figs. 3 and 4. Fig. 3 plots the equilibrium reaction rate of the first Zeldovich reaction. We see that the old reaction rate expression was extrapolated to high temperature, which resulted in an order of magnitude underprediction of the rate at high temperature. (Note that temperatures of interest in re-entry shock layers are typically over $10,000\,\mathrm{K}$.) Figure 4 plots the computed reaction rate at a constant temperature of $T = 14,000\,\mathrm{K}$ as a function of the vibrational and rotational temperatures. We see that lower internal energies suppress the reaction rate. Thus, there is an increase in the equilibrium reaction rate, but a decrease in the effectiveness of the translational temperature. This results in a small net increase in the NO formation rate at typical high-altitude re-entry conditions.

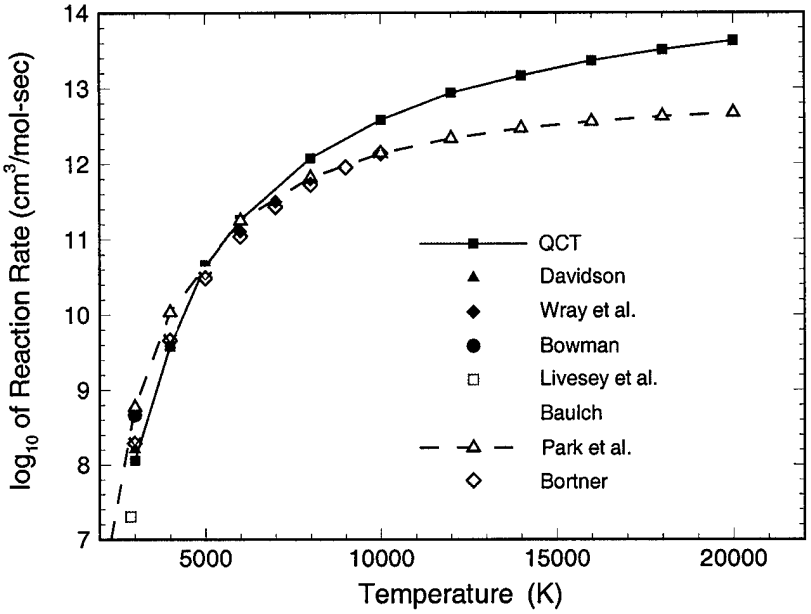

Figure 3. New equilibrium $N_2+O \rightarrow NO+N$ (QCT) reaction rate as compared to previous high-temperature data-fit and to experimental data.

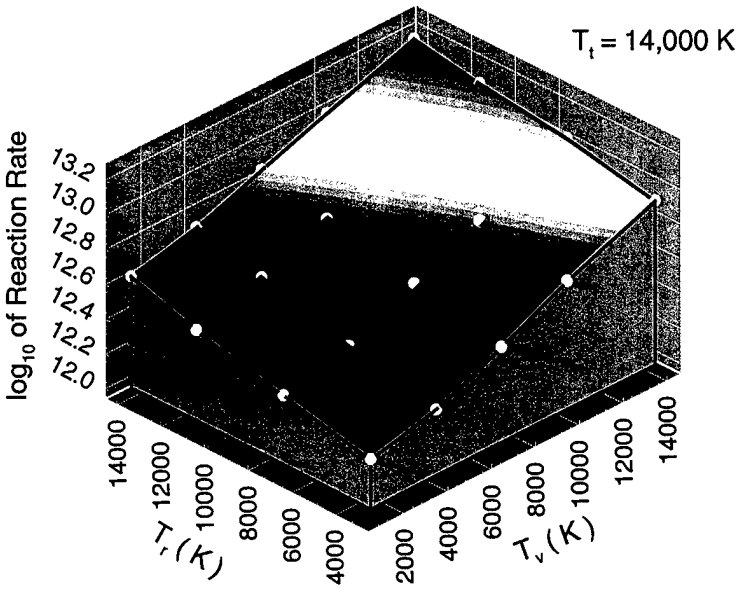

Figure 4. New nonequilibrium N_2+O $\rightarrow$ NO+N reaction rate at $T =$ 14,000 K as a function of the vibrational and rotational temperatures.

Summary of Radiation Modeling Results

Based on the computational chemistry results, we formulated an advanced model for nitric oxide formation, including the effects of thermal nonequilibrium on the reaction rates and the deposition of energy as a result of reactions. The model was implemented in both the continuum CFD code and in the DSMC method. To compare the effects of the improved modeling, we first compared the predicted signal to that obtained by the 230 nm photometers in the two flight experiments. We found that to within the knowledge of the free-stream density, temperature, and O atom number density, we could reproduce the experimental data at *all* altitudes where data are available. In general, the continuum formulation tends to slightly under-predict the data at high altitude, but under these conditions, the DSMC method gives very good agreement.

A more stringent test of the modeling involves comparison between the predicted wavelength-dependent radiation spectra and that measured in the experiments. For example, Figure 5 plots the experimental spectra measured from the stagnation region of the BSUV-2 experiment at two altitudes. These data are compared with the results of four different nitric oxide thermo-chemistry models. Essentially, these models increase in

complexity, with the Baseline model representing the state-of-the-art prior to our work. The other three models are summarized in Table 1, below.

The comparison between the spectra clearly illustrate how much better the improved models work. It is important to note that the Baseline model results have been normalized so that they match the experimental data at one wavelength. Thus, the comparison that we are making for the Baseline model only involves the *shape* of the predicted spectra. (Fig. 1 shows that the Baseline model is orders of magnitude in error in terms of its overall level.) The comparisons with the other models are not based on normalized values, making the comparisons much more difficult. Note that at the lower altitude (79 km), the Baseline model misses the reduction of peak heights with wavelength in the plotted spectral region, while the advanced models show a much better agreement. The differences are much more obvious in the high altitude comparison (87.5 km), where Models II and III do an excellent job of capturing the magnitude and the progression in the peak heights. Clearly the Baseline model and Model I are completely inadequate to describe the spectral features of this flow.

Table 1. Various models used to treat the Zeldovich reactions. QCT refers to the Quasi-Classical Trajectory method used to obtain the new Zeldovich reaction rates and energy deposition mechanisms.

	$N_2 + O \rightarrow NO + N$	$O_2 + N \rightarrow NO + O$
Model I	Rate: Park *et al.* NO energy disposal: average energy	Rate: Park *et al.* NO energy disposal: average energy
Model II	Rate: QCT NO energy disposal: QCT	Rate: Park *et al.* NO energy disposal: average energy
Model III	Rate: QCT NO energy disposal: QCT	Rate: QCT NO energy disposal: QCT

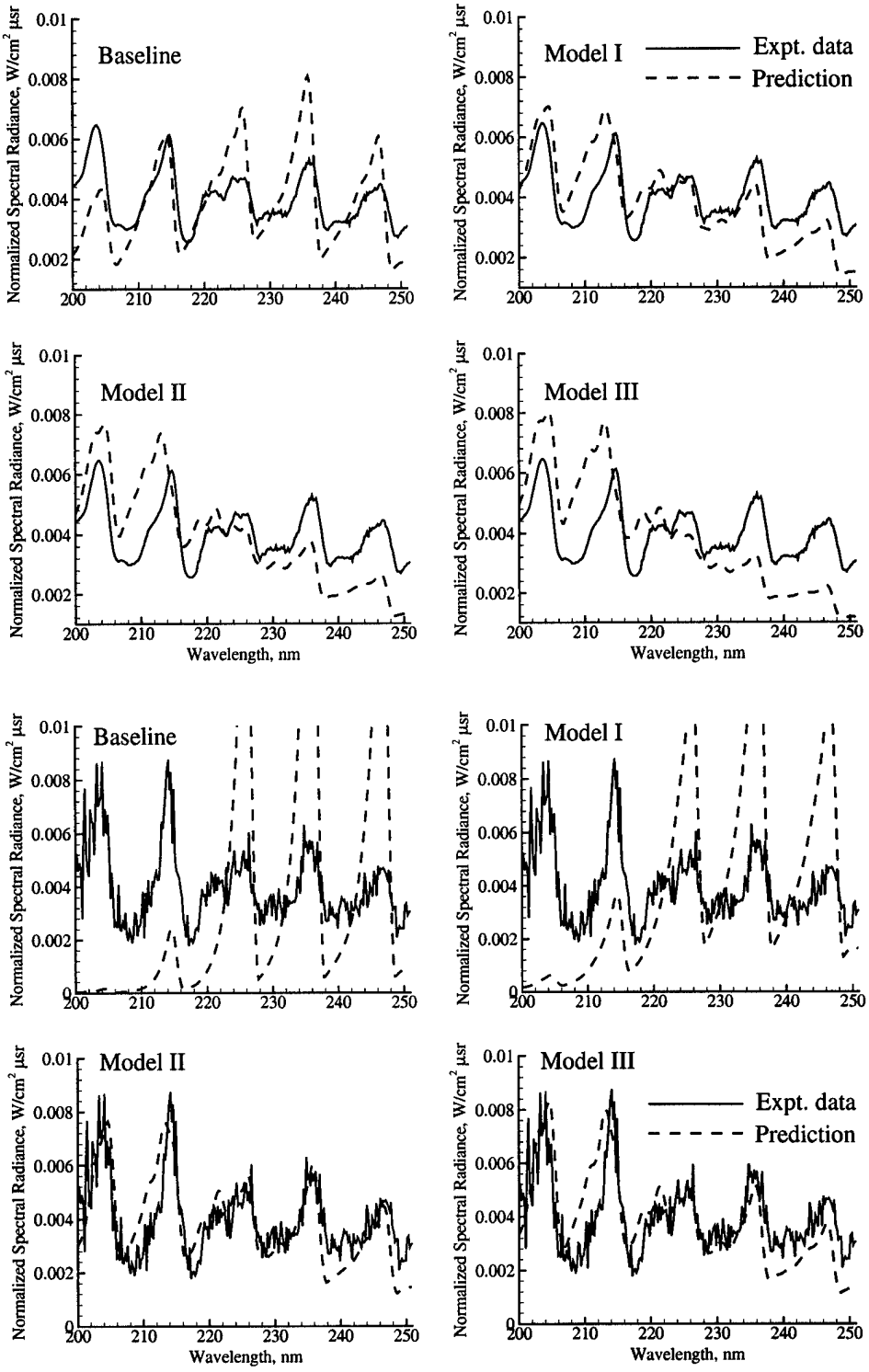

Figure 5. Comparisons of the spectra based on the flow field solutions with the BSUV-2 experimental data at two altitudes: 79 km (top) and 87.5 km (bottom).

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REPORT OF INVENTIONS

None.