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THEORETICAL STUDIES OF THE REACTIONS AND SPECTROSCOPY OF RADICAL SPECIES RELEVANT TO COMBUSTION REACTIONS AND DIAGNOSTICS

PROGRESS REPORT

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ABSTRACT

This report describes the use of our electronic structure algorithms to treat nonadiabatic processes relevant to combustion diagnostics and combustion reactions during the first nine months of Department of Energy grant DE-FG02-91ER14189 and outlines future work to be performed. During this period three problems have been addressed in detail: (i) the possibility of using photoionization spectroscopy to detect CH_3O, (ii) the lifetimes of the individual ro-vibronic levels in OH(v=3) a state that has been suggested as a fluorescence probe of OH produced in combustion environments and (iii) the basic mechanism for the spin-forbidden initiating step in the Fenimore mechanism for the production of NO in flame fronts, $CH(X^2\Pi) + N_2(X^1\Sigma_g^+) \rightarrow HCN(X^1\Sigma^+) + N(^4S)$.

TECHNICAL REPORT

Our research program focusses on studies of spin-forbidden and electronically nonadiabatic processes involving radical species that are relevant to combustion reactions and combustion diagnostics. To study the electronic structure aspects of these processes a unique and powerful system of electronic structure programs, developed over the past six years, the BROOKLYN codes, is employed. These programs enable us to address questions basic to the understanding of elementary combustion chemistry processes which are not tractable using more standard quantum chemistry codes. Particularly relevant to this research program are the capabilities to

(i) treat the spin-orbit interaction with in the context of the full microscopic Breit-Pauli approximation,

(ii) determine the interstate derivative couplings $f_\alpha^{IJ}(\mathbf{R}) = \left\langle \Psi_I^0(\mathbf{r};\mathbf{R}) \middle| \frac{\partial}{\partial R_\alpha} \Psi_J^0(\mathbf{r};\mathbf{R}) \right\rangle_{\mathbf{r}}$ which result in the breakdown of the single surface Born Oppenheimer approximation and

(iii) locate seams of actual/avoided crossings of potential energy surfaces of the same symmetry, and the minimum energy point on surfaces of intersection of potential energy surfaces of different spin-multiplicity.

We have used these methods to address problems in the following areas:

Spin-forbidden Radiationless Decay

(a) Spin-forbidden decomposition of $CH_3O^+(^3A_2)$

Motivated by conversations with Dr. J. Berkowitz at the Argonne National Laboratory we have considered[1] the feasibility of the spin-forbidden process

$$CH_3O^+(^3A_2) \rightarrow CH_3O^+(^1A') \rightarrow HCO^+(X^1\Sigma^+) + H_2(X^1\Sigma_g^+)$$

It has been suggested that this radiationless decay process limits the ability to detect CH_3O by photoionization methods. The barrier to this processes occurs at the minimum energy crossing point on the surface of intersection of the lowest $^3A''$ and $^1A'$ potential energy surfaces. The straightforward procedure that has been used in the past to locate the minimum energy point, is referred to as the indirect determination of the minimum energy crossing point. In the indirect method the crossing surface is first characterized and then its minimum is determined. This

procedure is computationally costly since for a system with N internal degrees of freedom (here 9) a crossing surface, or seam, of dimension N–1 must be determined and analyzed. Thus the determination of this point represents a significant computational bottleneck. However this bottleneck can be avoided. Fletcher[2] has shown that the minimum energy crossing point can be determined directly, that is, without prior determination of the crossing surface itself, by solving the following Lagrange-Newton system of equations:

$$\begin{bmatrix} \mathbf{W}^{IJ}(\mathbf{R},\lambda) & \mathbf{g}^{IJ}(\mathbf{R}) \\ \mathbf{g}^{IJ}(\mathbf{R})^{\dagger} & 0 \end{bmatrix} \begin{bmatrix} \delta\mathbf{R} \\ \delta\lambda \end{bmatrix} = -\begin{bmatrix} \mathbf{g}^{I}(\mathbf{R}) + \lambda \mathbf{g}^{IJ}(\mathbf{R}) \\ \Delta E_{IJ}(\mathbf{R}) \end{bmatrix} \qquad 1$$

where $\delta\mathbf{R} = \mathbf{R}' - \mathbf{R}$, $\delta\lambda = \lambda' - \lambda$, and the energy gradient $\mathbf{g}^{I}(\mathbf{R})$ and energy difference gradient $\mathbf{g}^{IJ}(\mathbf{R})$ are given by

$$g^{I}_{\alpha}(\mathbf{R}) = \frac{\partial E^{0}_{I}(\mathbf{R})}{\partial R_{\alpha}} \qquad 2a$$

$$g^{IJ}_{\alpha}(\mathbf{R}) = \frac{\partial E^{0}_{I}(\mathbf{R})}{\partial R_{\alpha}} - \frac{\partial E^{0}_{J}(\mathbf{R})}{\partial R_{\alpha}} = \frac{\partial \Delta E_{IJ}(\mathbf{R})}{\partial R_{\alpha}} \qquad 2b$$

and the second derivative matrix, $\mathbf{W}^{IJ}(\mathbf{R},\lambda)$, is given by

$$W^{IJ}_{\alpha\beta}(\mathbf{R},\lambda) = \frac{\partial^2 L_{IJ}(\mathbf{R},\lambda)}{\partial R_{\alpha}\partial R_{\beta}} = \frac{\partial}{\partial R_{\alpha}}\left[g^{I}_{\beta}(\mathbf{R}) + \lambda g^{IJ}_{\beta}(\mathbf{R})\right] \qquad 3$$

$W^{IJ}_{\alpha\beta}(\mathbf{R},\lambda)$ can be determined using a forward or a centered difference of $g^{I}_{\beta} + \lambda g^{IJ}_{\beta}$, that is:

$$W^{IJ}_{\alpha\beta}(\mathbf{R},\lambda) = \left\{\left[g^{I}_{\beta}(\mathbf{R}+\varepsilon\mathbf{I}^{\alpha}) + \lambda g^{IJ}_{\beta}(\mathbf{R}+\varepsilon\mathbf{I}^{\alpha})\right] - \left[g^{I}_{\beta}(\mathbf{R}) + \lambda g^{IJ}_{\beta}(\mathbf{R})\right]\right\} / \varepsilon \qquad 4a$$

or

$$= \left\{\left[g^{I}_{\beta}(\mathbf{R}+\varepsilon\mathbf{I}^{\alpha}) + \lambda g^{IJ}_{\beta}(\mathbf{R}+\varepsilon\mathbf{I}^{\alpha})\right] - \left[g^{I}_{\beta}(\mathbf{R}-\varepsilon\mathbf{I}^{\alpha}) + \lambda g^{IJ}_{\beta}(\mathbf{R}-\varepsilon\mathbf{I}^{\alpha})\right]\right\} / 2\varepsilon \qquad 4b$$

where $\mathbf{I}^{\alpha}$ is a unit vector along the direction R_{α}. In our implementation the gradient and energy difference gradient are evaluated- for MCSCF/CI wavefunctions- without recourse to divided difference differentiation, using analytic gradient techniques.[3] It is important to observe that

because analytic gradient techniques are used to evaluate the right hand side of eq. 1 *it is not necessary to limit the number of nuclear degrees of freedom considered in that equation.*

For the methoxy cation it was shown, using CI expansions as large as 2.5 million configuration state functions, that ΔE=15.4kcal/mol, where ΔE is defined as the difference between the energy at the minimum energy crossing structure, denoted MEX(^{3}A"–^{1}A'), and the energy at the minimum on the bound state potential energy surface. Thus this reaction provides a low energy decomposition pathway. Our calculations further showed that following the intersystem crossing onto the singlet surface the system will evolve to $HCO^+ + H_2$.

The spin-orbit interactions $H_{\perp}^{so}$ and $H_{\parallel}^{so}$, where

$$H_{\perp}^{so} = \left\langle \Psi_{2A'}(^3A'') \middle| H^{so} \middle| \Psi_{1A'}(^1A') \right\rangle \quad 5a$$

$$H_{\parallel}^{so} = \left\langle \Psi_{1A'}(^3A'') \middle| H^{so} \middle| \Psi_{1A'}(^1A') \right\rangle \quad 5b$$

and

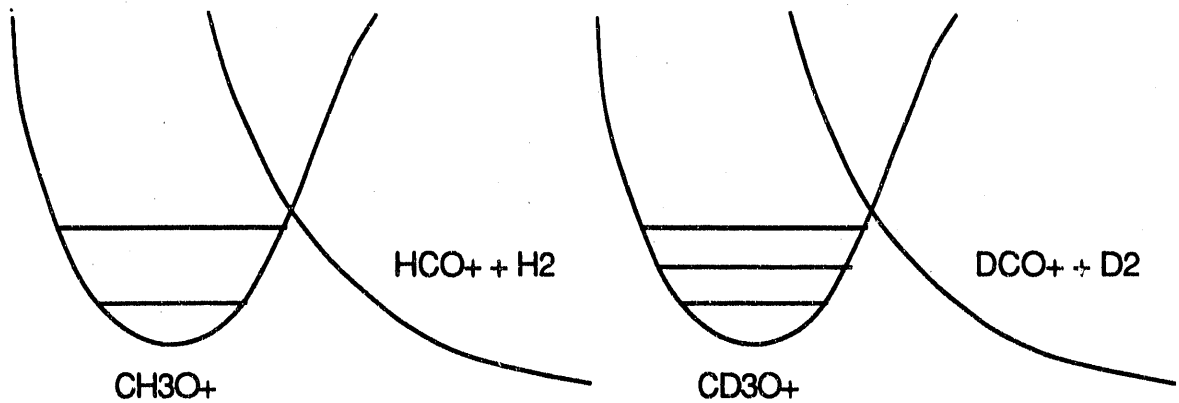
$$\Psi_{1A'}(^1A') = \Psi[^1A'(0)] \quad 6a$$

$$\Psi_{1A'}(^3A'') = i\,\Psi[^3A''(0)] \quad 6b$$

$$\Psi_{2A'}(^3A'') = i\,\{\Psi[^3A''(1)] - \Psi[^3A''(-1)]\}/\sqrt{2} \quad 6c$$

$$\Psi_{1A''}(^3A'') = i\,\{\Psi[^3A''(1)] + \Psi[^3A''(-1)]\}/\sqrt{2} \quad 6d$$

were determined at MEX(^{3}A"–^{1}A'). We found $H_{\perp}^{so}$=11.3cm^{-1} and $H_{\parallel}^{so}$=66.4cm^{-1}. Using an approximate Landau-Zener model, it was estimated that vibrational states with energies above the minimum energy crossing will intersystem cross within 1000 vibrational periods, that is 1000 passes through the intersurface crossing. Thus our calculations suggest the qualtitative picture illustrated below (the vibrational levels shown are for illustrative purposes only and are not -yet- based on actual calculations)

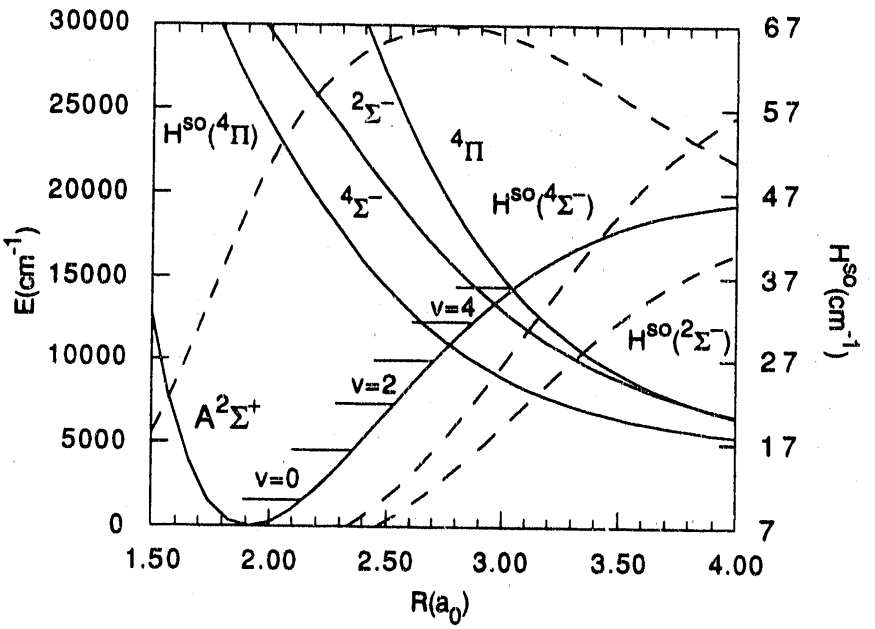


which is in accord with the experimental results of Ruscic and Berkowitz[4] who observed CD_3O^+ in photoionization experiments but were unable to observe CH_3O^+.

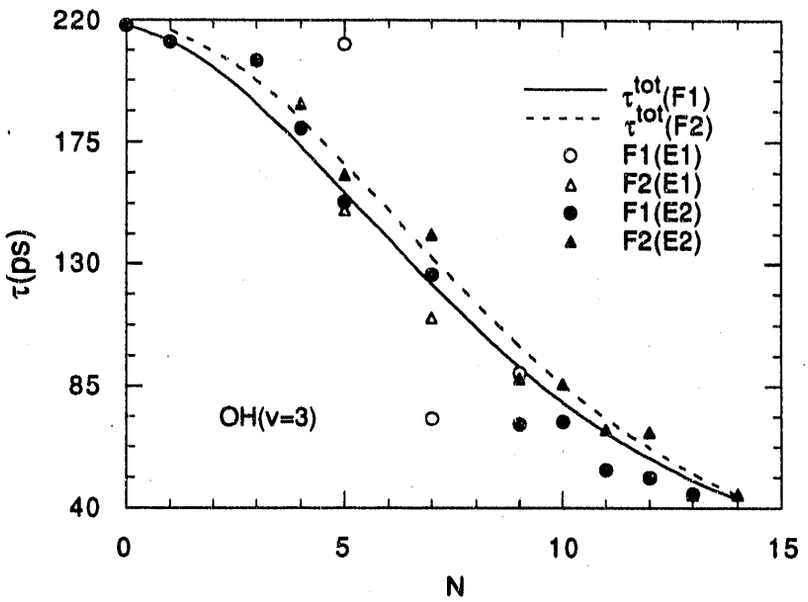
Decay rates for the predissociated levels, that is levels below the minimum energy crossing point energy, cannot be considered in this approximate manner and require a more complete treatment of the decay process. Calculations to determine the lifetime of these levels will be object of future work.

(b) Predissociation of the Individual rovibronic levels of $OH(A^2\Sigma^+)$

In situ detection of nascent OH is an important problem in studies of combustion processes. Recently several groups,[5, 6, 7] including the very recent work of Gray and Farrow at the Sandia Combustion Research Facility[6] and Crosley and co-workers are SRI International,[7] have considered using the strongly predissociated $OH(A^2\Sigma^+,v=3)$ state in a laser fluorescence detection scheme. This predissociation is induced by the $1^4\Sigma^-$ state and is thus spin-forbidden (see the following figure).



Reliable theoretical modelling of the predissociation process requires accurate $A^2\Sigma^+ \sim 1^4\Sigma^-$ spin-orbit couplings, which were not available. We have determined the requisite couplings and are modelling various aspects of this radiationless decay process. Our initial results[8] in this regard are summarized in the following figure which reports our total decay rate for OH($A^2\Sigma^+$, v=3, N, F_i) $\tau^{tot}(F_i)$ and compares it with the results of Gray and Farrow (E1) and Crosley and co-workers(E2). [The *relative* decay rates of Crosley were scaled to agree with our theoretical results for N=0.]



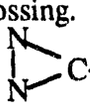
Spin-forbidden Chemical Reactions

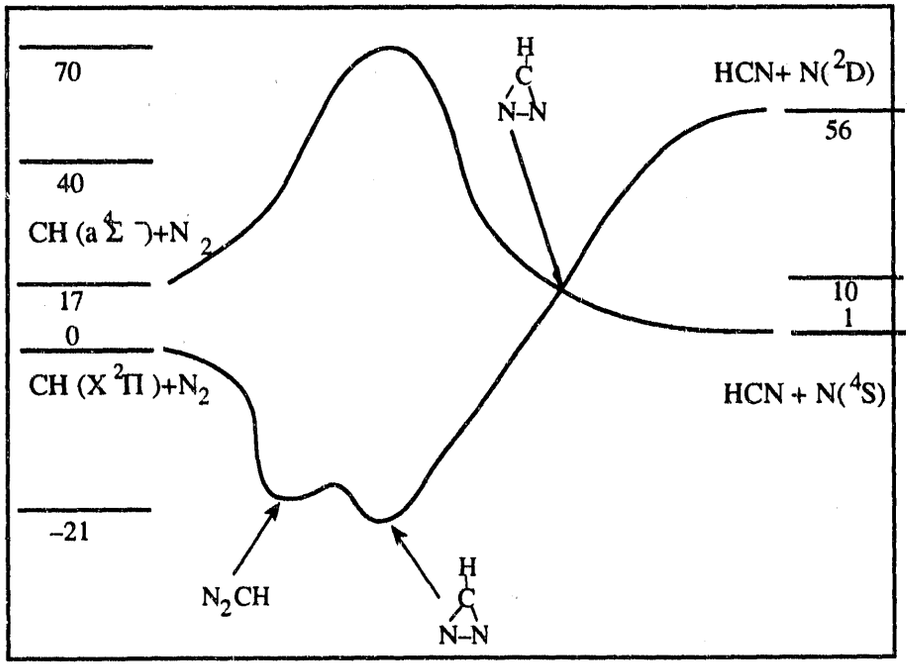
The spin-forbidden radical-molecule reaction

$$CH(X^2\Pi) + N_2(X^1\Sigma_g^+) \rightarrow HCN(X^1\Sigma^+) + N(^4S)$$

is important in the production of NO in flame fronts.[9] The rate constant for this reaction is difficult to measure.[10, 11] Previously as part of other funded research we had considered the doublet-quartet intersystem crossing in order to establish the feasibility of this reaction.

However because of the importance of this system in combustion models a more complete treatment of this reaction was deemed appropriate. Thus as part of this DOE funded research program we have, on the basis of MCSCF/CI calculations, developed[12] the following the intermediate complex driven model of this reaction. The intermediate complex model was first proposed by Tully[13] and of Zahr, Preston and Miller[14] to explain the efficiency of certain atmospheric quenching reactions including $N_2(X^1\Sigma_g^+)+O(^1D) \rightarrow N_2(X^1\Sigma_g^+)+O(^3P)$. Our calculations suggest that $CH(X^2\Pi)$ approaches $N_2(X^1\Sigma_g^+)$ approximately perpendicular to the the N_2 bond. Energy transfer from this relative translational mode to the N_2 stretch and other internal coordinates results in a metastable intermediate complex, with the approximate structure


. This metastable complex can repeatedly traverse the doublet-quartet crossing seam in the vicinity of the transition state which occurs at the minimum energy crossing point. In this way the intermediate complex facilitates the intersystem crossing. The geometrical arrangement at the minimum energy crossing point also has the structure  except that the N-N bond is more highly stretched. Those molecules which cross onto the quartet surface proceed, via asymmetric N-N motion, exoergically and irrevocably to the products $HCN(X^1\Sigma^+) + N(^4S)$, see the following figure.



FUTURE PLANS

During the forthcoming year we plan to pursue some needed extensions of the research discussed above.

For the $CH(X^2\Pi) + N_2 \rightarrow HCN(X^1\Sigma^+) + N(^4S)$ reaction we plan to determine the requisite potential energy surfaces based on high quality *ab initio* electronic structure calculations in order to further quantify the model for this reaction discussed above. These surfaces will then be used together with trajectory surface hopping techniques to consider the rate constant for this

reaction. Similarly additional calculations of the potential energy surface for the CH_3O^+ system are planned in order to be able to quantify the predissociation rates for the bound levels.

In the OH/OD predissociation problem we will consider the predissociation of the v=4 level. When compared with the v=3 level, for v=4 much less precise lifetime data is available. Our initial treatment of this predissociation showed that for OH(v=4) three dissociative states the $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$ states contribute to the predissociation of the $A^2\Sigma^+$ state whereas for the v=3 level only the $^4\Sigma^-$ state contributes to the predissociation. This suggests that the golden rule analysis used in our previous treatment must be replaced with a more precise analysis based on multichannel quantum scattering. We will use a modified version of our existing log-derivative quantum scattering program to consider the v=4 predissociation.

As outlined in our original proposal we intend to consider nonadiabatic effects in excited Rydberg states accessed in resonance enhanced multiphoton ionization (REMPI) detection schemes of flame species including the C_2 and HCO systems as well as other radicals present in combustion environments including C_2H and CH_2 .

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†Reprint enclosed

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