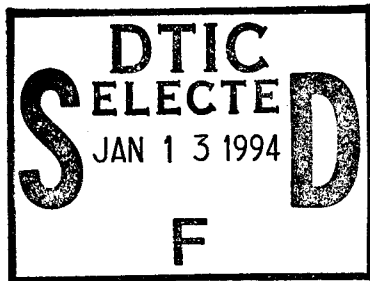


Properties of New Materials Relevant to Energy and Fuel Research



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This technical report has been reviewed and is approved for publication.



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Summary

The work represents a contribution toward the quantitative understanding of certain energy trapping and release processes of the molecular level for novel compounds. In particular, it has dealt via advanced computations with questions of formation, properties as equilibrium and at transition states, and of spontaneous or laser-induced fragmentation of unusual molecules existing because of local minima on repulsive surfaces. Such molecules are a number of new nonclassical hydrogen complexes (E.g. OBeH_2 , F_3AlH_2 , $\text{F}_4\text{Mg}_2\text{H}_2$). For diatomic volcanic and excimer states, newly developed ab initio computational methods were applied for obtaining the time-dependent probabilities for a number of multiphoton dissociation and excitation processes.

"Properties of new materials relevant to energy and fuel research"

C.A. Nicolaides

Our research activities were developed along two major directions (I and II below). The first was oriented toward the prediction, through concepts of chemical binding and reliable advanced computations, of new, nontransition metal-containing compounds capable of trapping hydrogen in molecular form. Examples of such molecules are the F_3AlH_2 [1] and $OBeH_2$ [2], which are formed in a local minimum of the ground potential energy hypersurface.

The second direction involved the development of theory and computational methods for the reliable solution of the time-dependent Schrödinger equation (TDSE), which is necessary for the rigorous study of processes of energy exchange induced by the interaction of short laser pulses with molecules [3-5]. Furthermore, we started the development of close-coupling scattering methods that can be used for the calculation of certain multichannel reaction problems involving volcanic states [6]. More specifically, what was accomplished and published is summarized below:

I. Non-classical hydrogen complexes of nontransition metals.

Two types of studies were carried out. The first dealt with the prototypical $OBeH_2$ molecule [2], for which extensive calculations were carried out on the ground state potential energy surface in order to locate its isomers, the local and global minima of this surface, their energetics and the possible reaction paths going from one to the others.

All calculations were performed using state-of-the-art analytic gradient and geometry optimization techniques. The basis sets employed were judiciously chosen, based on wide experience gained by similar calculations on other molecules, to be large enough to provide reliable energetics and small enough to allow the project to be tractable. The level of theory was chosen to be that of the Fermi-Sea-multiconfiguration-self-consistent-field approximation, a level of theory ideally suited for this type of calculation.

The mapping of this PES, carried out over a period of several months and leading to results which provide insight into the workings of intramolecular rearrangements,

showed the existence of five isomers (or minima) on this surface, namely, on order of increasing energy, H-O-Be-H, H₂O+Be, OBeH₂. It was shown that trapping of molecular hydrogen by BeO to form OBeH₂ is possible and *barrierless*, but only if the H₂ approaches BeO at right angles. Should this happen, it was also shown that this local minimum is stable enough to exist. The most interesting finding, however, was that from OBeH₂ one can only go to the global minimum of the surface, i.e. H-O-Be-H, thus releasing a considerable amount of energy (more than 70 Kcal/mole).

The second series of studies involved the prediction of the existence (or nonexistence) and of properties of complexes involving light metal atoms and H₂ in molecular form [1,7].

The technique of Moller-Plesset Perturbation Theory to second order was used, in conjunction with fully analytic gradient and second derivative methods. Location of stationary points was done with no constraints on the internal geometrical parameters other than symmetry where applicable, and the stationary points were characterized via full vibrational analysis in order to verify that the structures of interest correspond to true local or global minima of the potential energy surface.

Following the initial results on alkaline earth -H₂ cations, [8], the possible structures AlH₂⁺, AlH₂²⁺ and AlH₂³⁺ were investigated. AlH₂²⁺ is found to be a non-classical type complex with a binding energy of 20.6 kcal/mol. AlH₂⁺ is also similar, but extremely weakly bound. The search for a complex containing two metal atoms bound by a metal-metal bond on the other hand, reveals that no stable Al₂H₄²⁺ structure exists in the gas phase, contrary to B₂H₄²⁺ which is a stable classical hydride.

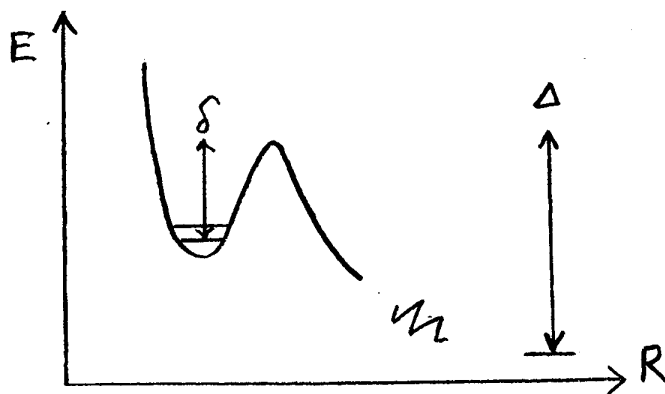
As regards the research for neutral H₂ complexes, extensive calculations were performed in order to locate complexes of magnesium and aluminum fluorides. A planar C_{2v} F₂ Mg...H₂ and an eclipsed C_s F₃Al...H₂ structure were found to be stable structures in the gas phase, by about 2.4 and 2.7 kcal/mol respectively (at the MP2 level of theory), when all corrections due to basis set superposition error (BSSE) are taken into account. In both cases, H₂ retains its molecular nature to a great extent, the red shifts in the H-H harmonic stretching frequency being 137 and 120 cm⁻¹ respectively. Full structural and vibrational analysis was performed on both complexes, providing useful predictions to facilitate the experiment detection and characterization.

High quality computations were also performed on the dimer Al₂F₆, for which the theoretical investigations reported in the literature are extremely approximate and very few experimental data have been published. Preliminary investigations however, using analytic gradient methods, did not reveal the existence of any H₂ complexes with this dimer.

Finally, magnesium fluoride dimers (Mg_2F_4) and their H_2 complexes were studied. Two stable forms were found, having D_{2h} and C_{3v} symmetries, for which the harmonic vibrational and infrared intensities were calculated [7].

II. Laser pulse induced multiphoton dissociation of volcanic states.

Molecules which exist in local minima on overall repulsive surfaces can produce excess energy upon bond breaking. This can be seen from the plot below, representing a one-dimensional section of the "volcanic" hypersurface of such molecules or a diatomic molecule.



The break-up energy which is required (δ) is smaller than that which is released (Δ).

A technologically practical way to induce such fragmentation, is to expose molecules to strong laser pulses of IR frequency. In order to study this phenomenon rigorously, we developed a general ab initio method for solving the corresponding TDSE [3]. Applications have thus far been made to BeH^{++} [3] and NO^{++} [4], both of which have volcanic ground state potentials. In the study of BeH^{++} interacting with a laser pulse, the intensity was in the range 10^{10} - 10^{11} W/cm^2 , the frequency that of the CO_2 lasers and the duration 0.44 ps. In spite of the relatively low intensities, the known phenomenon of above threshold dissociation (ATD) was obtained, as well as a new one, which we named below threshold dissociation (BTD), since it requires fewer photons than expected from energy considerations. The reason for these results is the volcanic shape of the potential energy of BeH^{++} , which supports a relatively small number of vibrational quasi-discrete levels, of which the two near the barrier top mix heavily with the adjacent dissociation continuum. On the other hand, in NO^{++} [4], both the lowest two states ($X^2\Sigma^+$ and $A^2\Pi$) exist in local minima and offer a real model of low-lying embedded vibrational spectra, where both the discrete and the continuous parts couple via the electric dipole interaction. It was found that this coupling enhances the dissociation.

tion through the $A^2\Pi$ state, which controls the dynamics of the dissociation.

Finally, the possibility of solving ab initio the TDSE for real systems gave us the opportunity of computing for the first time the formation of excimer states of noble gas hydrides (HeH, NeH, ArH), and of HeF, by absorption of femtosecond pulses from the repulsive ground states [5]. Additional information was obtained regarding energy transfer processes in these excited states. For example, starting the photoreaction in HeF from the first excited repulsive state $1^2\Pi$ with a pulse of frequency 4eV, allows an experimentally verifiable probability of obtaining bound-continuum emission at about 1320 Å (9.4 eV).

In conclusion, considerable progress was made during this project (see reference list) in the development of advanced theory and computational methods and in the ab initio understanding of certain materials and processes related to energy storage, release and transfer at the molecular level, taking into account the interaction with pulsed lasers as well. Our efforts adhered to the original research objectives but also expanded into the rapidly developing field of time-dependent pulsed laser induced molecular dissociation.

Some of this work was presented in lectures at Universities and Laboratories of Europe and the USA, (including Los Alamos and the Florida Solar Energy Center), and at International meetings. Finally, the grant allowed the partial support of my research associates Drs. Mercouris, Petsalakis, Simandiras and Valtazanios.

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