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Theoretical Investigation of Energy Storage in Atomic and Molecular Systems: Metastable Molecular Fuels

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NOTICE

FOREWORD

SRI International, Menlo Park CA submitted this final report on completion of Contract F04611-86-C-0070 with the Astronautics Laboratory (AFSC), Edwards Air Force Base CA. The AL Project Manager was Lt Pete Dolan.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.

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Ion-pair species bound by the coulomb attraction between a stable positive and stable negative ion have been investigated theoretically as candidate high-energy fuels that could form the basis of new propulsion schemes. Theoretical results for H3O, Li3H, and H3F are presented along with specific impulse (Isp) predictions based on calculated energies. The ion-pair local minimum on the first excited potential surface of H3O is found to be unstable with respect to dissociation to $H_2 + H + O$. The ion-pair state of H3F has a doubly degenerate imaginary frequency. These results support the general conclusion that ion-pair states based on the H_3^+ cation will not be stable because back-charge transfer to H_3^+.. leads to neutral H3, which is unstable with respect to $H_2 + H$. The ion-pair state of Li3H is found to be a local minimum with, however, a very small barrier to conversion to the lower energy planar form. Even the lowest energy form of Li3H as an additive to hydrogen is predicted to provide a 16% improvement in Isp.

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CONTENTS

SUMMARY

Metastable molecular fuels, high-energy long-lived molecular species that do not decay by radiation, tunneling, or other means when isolated in vacuum, have been proposed as the basis for possible new propulsion schemes. This theoretical project has been devoted to examination of ion-pair species bound by the coulomb attraction between a stable positive and stable negative ion as possible candidate fuels. Theoretical results for H_3O, Li_3H, and H_3F are presented in this report along with specific impulse predictions based on calculated energies.

The greatest effort was directed at the H_3O molecule, which was selected as the first candidate ion-pair system because of the significant electron affinity (1.46 eV) of the oxygen atom. Minimum geometries and transition states on the first two doublet surfaces of H_3O have been obtained by multiconfiguration self-consistent field (MCSCF) analytic gradient techniques, and the correlation diagram connecting these states to the separated fragment asymptotes to which they fragment has been constructed. While the energetic ion-pair state was found unstable, the possible stability of the lowest state of H_3O has been the subject of significant experimental interest. Theoretical results have been related to experimental reports of metastable D_3O.

While there exists a region of the lowest energy surface that may be described as an ion-pair, our results have shown that the ion-pair is not even a local minimum on that surface. The ion-pair minimum identified as a local minimum on the excited 1 ^2E surface in C_{3v} symmetry is not stable in lower symmetry and is predicted to dissociate without an energy barrier to $H_2 + H + O$. This observation has been qualitatively explained by back-charge transfer from O^- to H_3^+, leading to neutral H_3, which is unstable with respect to $H_2 + H$.

In contrast, the Li_3H molecule is more likely to exist as a stable ion-pair because both Li_3^+ and Li_3 are bound species. As anticipated from this argument, the ion-pair conformation is found to be a local minimum with all real frequencies on the lowest potential surface of Li_3H. However, there exists a global planar minimum 20 kcal/mol lower in energy and the barrier height for conversion of the ion-pair state to the planar form is predicted to be only 1.3 kcal/mol.The correlation diagram for Li_3H has been determined.

In contrast to H_3O, the lowest states of Li_3H lie below all possible fragment energies. While the lowest state of Li_3H is most definitely stable, it is not particularly energetic.

Calculations of the minima and frequencies of the ion-pair state of H_3F support the conclusion that ion-pair states based on the H_3^+ cation are not stable with respect to back-charge transfer.

The goal of this project was to identify energetic molecular states that might serve as the basis of new propulsion schemes. To estimate the performance of these new metastable molecules, the specific impulse (I_{sp}) was calculated for each metastable molecule. The I_{sp} calculations assumed that metastable molecules (1) could be stabilized, (2) used the same exhaust conditions, and (3) did not optimize I_{sp}. Metastable D_3O as a monopropellant is predicted to provide a 7% improvement over H_2/O_2 under the same conditions. Because the ground state of Li_3H lies more than 30 kcal/mol below LiH + Li_2, Li_3H as a fuel does not have a favorable I_{sp}. However, Li_3H as an additive to H_2 in the ratio $Li_3H:H_2:O_2$ of 5:30:4 is predicted to provide a 16% improvement. Use of Li_2H as an additive is estimated to produce a 20% improvement.

INTRODUCTION

The energy density of today's rocket propellants severely limit rocket payloads and mission capability. For example, no matter how efficient the engine, a single stage rocket will always have a negative payload. Therefore, novel concepts that might serve as the basis of new propulsion schemes are of great interest. One concept that has recently been considered is the use of metastable molecular fuels. Metastable molecules are long-lived molecular species that do not decay by radiation, tunneling, or other means when isolated in vacuum.

The specific impulse, I_{sp}, which is proportional to the square root of the ratio of the heat of reaction to the molecular weight of the products, is the figure of merit for evaluating propulsion reactions. Therefore, ideal rocket propellants are compounds with high energy content which form low molecular weight products. This requirement virtually restricts the candidate species for metastable molecular fuels to molecules composed of first-row atoms.

Theoretical prediction,[1] several years ago, of an extremely energetic state of H_4 initially excited great interest. With very high energy and low molecular weight, H_4 appeared to be a promising molecular fuel. However, detailed theoretical study by several groups[2-4] during the last two years has led to the conclusion that the predicted state of H_4 is likely to have an extremely short lifetime. Nonetheless, the serious examination of the H_4 system has provided valuable insight that can guide the selection and study of future candidate molecules.

Tetrahydrogen is only one example of a class of excited compounds that might be termed ion-pair states because the stable geometry is predicted to resemble an H_3^+ ion in an equilateral triangle with the H^- ion above the center. The fate of an ion-pair species, once formed, will depend sensitively on the details of the potential surfaces that govern decay processes such as optical transitions, predissociation, and internal conversion. Thus, it is worthwhile to investigate various potential ion-pair energetic species to find the case that is most stable. This report presents results of theoretical studies of candidate ion-pair species composed of first-row atoms.

We expect the strength of the ion-pair bond to depend on the ability of the anion to remain negatively charged, i.e., on the electron affinity of the corresponding neutral. Because the oxygen atom has an electron affinity[5] of 1.46 eV, nearly twice that of atomic hydrogen, H_3O was selected as the first candidate system. Significant effort was devoted to this system, with the two-fold goal of (1) characterizing as completely as possible the minima and barriers on the low-lying potential surfaces of this prototype ion-pair system and (2) developing and validating theoretical strategies that can be applied to other systems. While the ion-pair state of H_3O is not predicted to be stable, our study examined other portions of the potential surface, and addressed the metastability of the lowest state ($1^2A'$).[6-11]

Two other ion-pair state molecules, Li_3H and H_3F, were also examined. We have considered the Li_3H system as an example of an ion-pair based on a different cation. In addition to addressing the general question of when can we expect the coulomb interaction to dominate molecular bonding, our work on Li_3H has proved relevant to the suggestion that addition of Li would improve the hydrogen-oxygen fuel if the technical problem of Li metal formation could be overcome. Since fluorine has the largest electron affinity of any first row element (3.4 eV),[5] the H_3F ion-pair state was also evaluated.

This report summarizes the results of *ab initio* calculations on H_3O, Li_3H, and H_3F and presents some general conclusions with respect to stability of ion-pair species. Details of the theoretical calculations are given in the resulting publications, which are attached as appendices. The specific impulse to be expected for H_3O and Li_3H, the former as a monopropellant and the latter as an additive to H_2, has been predicted based on the calculated heats of formation. Tables which summarize the theoretical performance of these fuels are provided in the section entitled Calculations of Specific Impulse.

CALCULATIONS OF ION-PAIR STATES

This theoretical project was devoted to study of ion-pair species bound by the coulomb attractic· between a positive and negative ion as possible candidate fuels. The greatest effort was directed at the H_3O molecule, which was selected as the first candidate system on the basis of the significant electron affinity[5] (1.46 eV) of the oxygen atom. Results obtained for H_3O, Li_3H, and H_3F systems are summarized below.

POTENTIAL SURFACES OF H_3O

Features of the two lowest doublet potential surfaces of H_3O, minima and transition states, are illustrated in Figure 1, in which the separated fragment asymptotes to which they dissociate are also indicated. Geometries have been optimized by multiconfiguration self-consistent field (MCSCF) analytic gradient techniques, and large-scale multireference configuration interaction (CI) calculations have been used to obtain energy separations. The calculations and conclusions are described in detail in a manuscript[12] that has been published in the *Journal of Chemical Physics* and is attached as Appendix A.

While there exists a region of the lowest energy surface that may be described as an ion-pair, our results have shown that the ion-pair is not even a local minimum on that surface. The ion-pair minimum identified on the excited 1^2E surface in C_{3v} geometry (shown by a dashed line in Figure 1) is a local minimum. It is, however, not stable in lower symmetry and is predicted to dissociate without an energy barrier to $H_2 + H + O$. This observation has been qualitatively explained by noting that the neutral H_3 is not a stable species. Therefore, any back-charge transfer from O^- to H_3^+ will lead to the neutral H_3, which is unstable with respect to $H_2 + H$.

In agreement with previous work,[13] we find the lowest state of H_3O may be characterized as an H_3O^+ core surrounded by an oxygen 3s Rydberg electron. This finding supports the inclusion of the H_3O molecule in a recent discussion by Herzberg[14] of hypervalent hydrides that may be expected to exist as Rydberg molecules because of the stability of the corresponding ion. As shown in Figure 1, the energy of the lowest state of

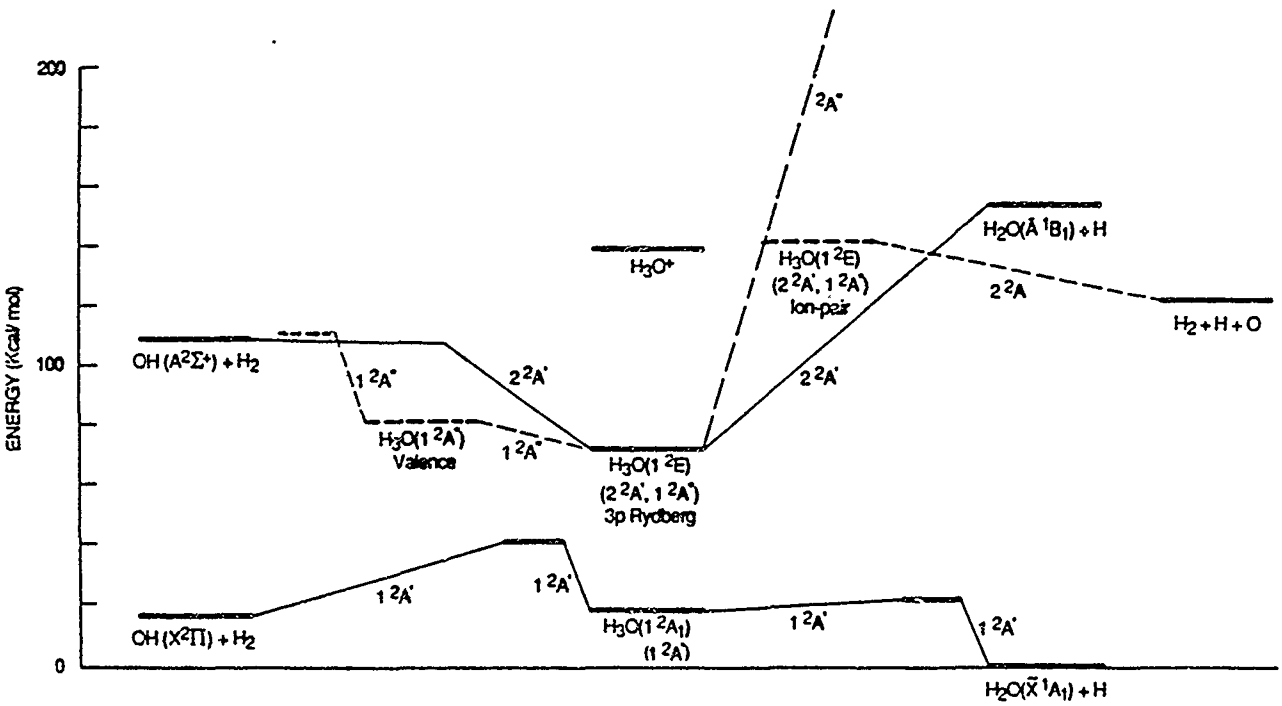

Figure 1. Minima and transition states for the H_3O system obtained in this work. Energies are given relative to H_2O + H. The 1^2E ion-pair state (dashed) dissociates without a barrier to H_2+H+O. The dashed transition state on the 1 $^2A''$ potential (labeled valence) surface connects to the OH+H+H asymptote (not shown).

H_3O is clearly above that of the asymptotes, $OH + H_2$ and $H_2O + H$. The stability of the $H_3O(1^2A')$ state depends on the barriers in the potential energy surface to dissociation.

The present work confirms the understanding obtained previously,[13] i.e., that the vibrationless potential of $H_3O(1^2A')$ has a very small barrier, 3.58 kcal/mol according to the present calculations, for dissociation to $H_2O + H$. Including zero-point energy, a barrier of 0.4 kcal/mol is predicted for this dissociation. Using the ratio of masses to estimate the vibrational frequencies for D_3O, we estimate a barrier of 1.3 kcal/mol for dissociation of D_3O.

There has been significant experimental interest[6-11] in characterizing the H_3O system and in establishing the metastability of the lowest state. Although an earlier mass spectrometric investigation[8] reported a lifetime of at least 1 μs for both H_3O and D_3O, the work of March and Young,[9] by a very similar experimental technique leads to the conclusion that H_3O is not stable. Gellene and Porter[6] have reported observation of metastable D_3O with a lifetime > 0.6 μs but found no evidence of H_3O. Our prediction of a 1.3 kcal/mol dissociation barrier for D_3O, but only a 0.4 kcal/mol barrier for H_3O, may be consistent with this report. The energy of the lowest state of H_3O with respect to H_2O + H is being probed experimentally by Devynck and Peterson[10] in this laboratory. (These workers are also investigating the D_3O isotope.) Preliminary results are in good agreement with the 23 kcal/mol excitation energy of H_3O above $H_2O + H$ predicted in this work. A more complete understanding of this system is expected from an experiment with photoionization detection which will establish the energy, with respect to the ion, of the state being formed. Such experiments are also under way in this laboratory.[10,11]

CALCULATIONS ON Li_3H

As discussed specifically for H_3O, back-charge transfer is now thought to limit the stability of any ion-pair species with H_3^+ as the positive ion. Michels[15] has suggested that Li_3H may be a more attractive candidate because both Li_3^+ and Li_3 are stable species. Preliminary calculations by Michels and Montgomery[15] support the stability of ground state Li_3H. We therefore studied the low-lying states of Li_3H using a similar computational procedure to that followed for H_3O and established the correlation diagram linking Li_3H states to the $LiH + Li_2$, $Li_2H + Li$, and $Li_3 + H$ asymptotes.

In agreement with a preliminary report[15] and with the recent study of Montgomery et al.,[16] we find a local minimum with all real vibrational frequencies on the lowest potential surface, the $1^1A'$, at the C_{3v} symmetry pyramidal geometry. Details are provided in the resulting publication attached as Appendix B.[17] Analysis of the wavefunction indicates substantial mixing of ion-pair and valence character at this pyramidal geometry. The Li-Li bond length of 5.173 a_0 for Li_3H is ~0.7 a_0 shorter than the corresponding bond length in Li_3^+, in contrast to the case for H_3O, where the ion-pair state was found at the H-H separation of H_3^+. The Li-Li bond lengths in the C_{2v} structure of Li_3 ($^2A_1$), to which this state correlates, are longer as well.

More important, however, there exists a planar minimum 20.3 kcal/mol lower in energy on the lowest singlet potential surface, as shown in Figure 2. We also optimized the transition state for conversion of the pyramidal form to the planar geometry that is predicted to have a low imaginary frequency of 120 i cm^{-1}. The transition occurs at a very modest geometrical distortion from the pyramid, with a calculated barrier height of 1.3 kcal/mol including zero-point energy. This result is in agreement with the recent work of Montgomery et al.,[16] who found the transition state at values between <1 kcal/mol above and 0.05 kcal/mol below the pyramidal minimum. These results include zero-point energy, and depend on the basis set and level of calculation).

The stability of the Li_3H ($1^1A'$) ion-pair should be considered to be problematical because of this low or nonexistent barrier. The lowest triplet state has a planar minimum geometry that lies 17.9 kcal/mol above the singlet ground state. The triplet does not have a local minimum in a pyramidal geometry.

As shown in Figure 2, in contrast to the case for H_3O, the singlet and triplet states of Li_3H lie below all possible separated fragment asymptotes. Figure 2 also includes the second state of each symmetry at the geometry of the ground state. The energies are of qualitative reliability only. These states are predicted, however, to be bound with respect to the LiH + Li_2 asymptotes to which they correlate.

The prediction of a true minimum on the $1^2A'$ surface (all real frequencies) at the C_{3v} geometry of mixed ionic and covalent character supports the original suggestion that because of the stability of Li_3 and Li_3^+, back-charge transfer will not limit the stability of Li_3H with respect to dissociation. Unlike the H_4 and H_3O cases, there is in this molecule a lower energy planar form. Given the very low calculated barrier to interconversion, the pyramidal local minimum is predicted to be unstable relative to the global planar minimum. While the lowest state of Li_3H is most definitely stable, it is not particularly energetic.

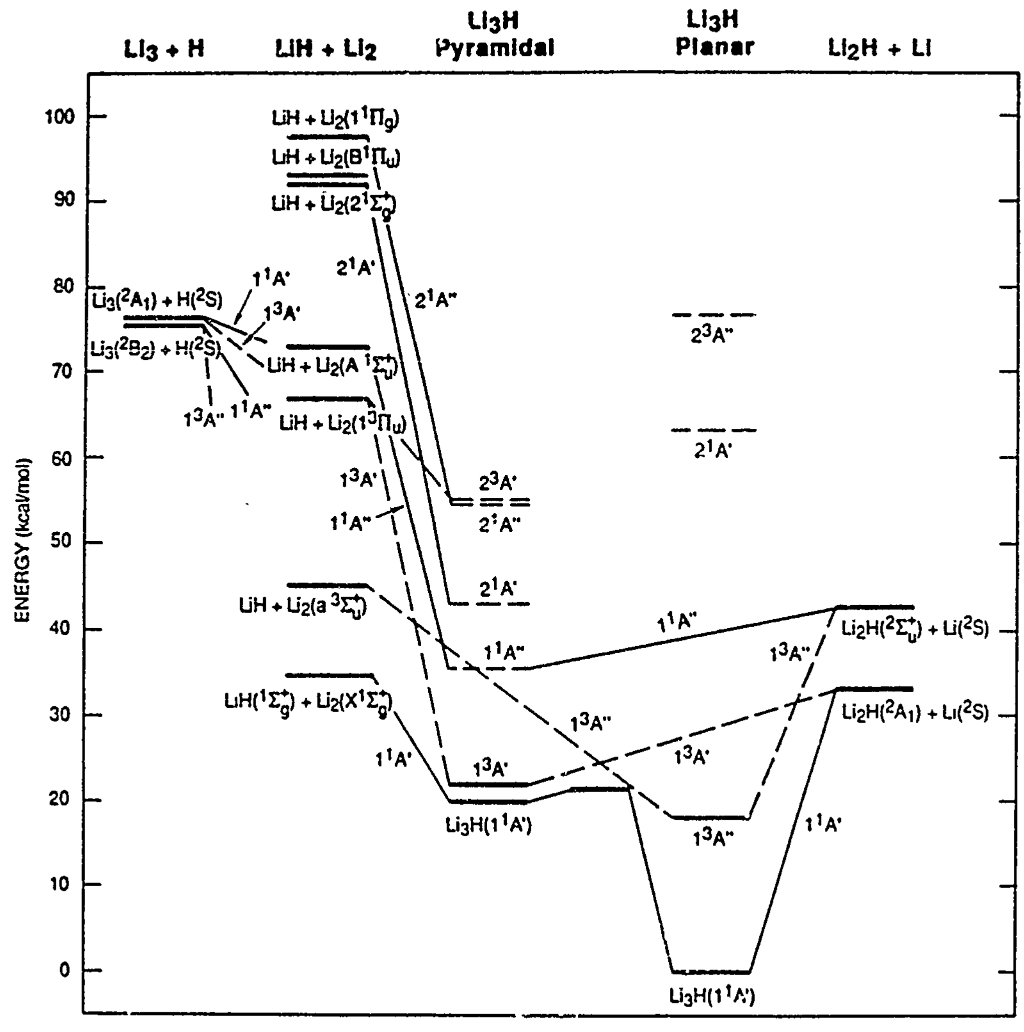

Figure 2. Correlation diagram linking the states of Li_3H to those of Li_3 + H and Li_2H + H, drawn in Cs symmetry using calculated energies. The second state of each symmetry has been calculated at the geometry of the lower state.

ION-PAIR STATE OF H_3F

The goal of the calculations on H_3F was to conclusively demonstrate whether back-charge transfer forming the dissociative ground state of H_3 will always prevent stability of an ion-pair state with H_3^+ as the cation, as indicated by the information on H_3O and H_4. Since fluorine has the largest electron affinity of any first-row atom (3.4 eV)[5], fluorine was expected to be the most favorable anion. Calculations were limited to determining the optimized geometry and harmonic frequencies of the ion-pair state of H_3F and a brief search for the global minimum on the lowest potential surface. In order to obtain results as rapidly as possible, preliminary optimization was performed at the self-consistent field (SCF) level.

Optimized geometries and frequencies are summarized in Table 1. The F atom basis set was taken from the work of Bauschlicher and Taylor[18] on the electron affinity of the fluorine atom. The qualitative conclusions presented here are independent of the basis set and type of calculation. The C_{3v} symmetry pyramidal minimum of the ion-pair state, which is found for an H-H separation very close to that of H_3^+ has a doubly degenerate E-symmetry imaginary frequency. At the SCF level, distortion of this geometry according to the normal modes corresponding to these imaginary frequencies leads to optimization of a very slightly bound van der Waals complex of H_2 and HF. Two minima very close in energy are found; in one of them the H_2 is attached to the hydrogen end of HF and in the other to the fluorine. The H_2--FH result is in reasonable agreement with the theoretical result reported by Sapse.[19] The van der Waals complexes are predicted to be bound by <1 kcal/mol at the SCF level. They have no energy content.

Although the study was not carried through to convergence at the MCSCF level, similar results are indicated. As shown in Table 1, at the MCSCF level the C_{3v} symmetry ion-pair state has a doubly-degenerate imaginary frequency in agreement with the SCF prediction. Preliminary results indicate that MCSCF optimization will lead to the van der Waals complex, in agreement with the SCF result. No stable ion-pair state of H_3F could be found.

The calculations on H_3F reported here support the conclusion that the H_3^+ cation does not form stable ion-pair states.

Table 1.

H_3F GEOMETRIES AND FREQUENCIES

	6-31G*/SCF	6-311G**/SCF	DZP+[b]/MC
Geometry[a] (C_{3v})			
H - H	0.851	0.857	0.862
F - H	1.633	1.665	1.696
d	1.557	1.590	1.620
Frequencies			
E	2052i	1786i	1750i
A_1	1194	1135	1059
E	2810	2914	2780
A_1	3598	3604	3593
Total energy[c]			
H_3F	-100.916774	-100.986778	-101.051231
H_2 + HF	-101.1297[d]		
H_2 - HF	-101.1306	-101.180[e]	

a. Distances Å, d=vertical distance from F to H_3 plane.
b. F basis set of Bauschlicher and Taylor, Reference 18.
c. Energies in hartrees.
d. Sapse, Reference 19.
e. Approximate energy - not completely converged.

CALCULATIONS OF SPECIFIC IMPULSE

The goal of this project is to identify energetic molecular states that might serve as the basis of new propulsion schemes. It is therefore valuable to estimate the specific impulse (I_{sp}) that could be expected from the species investigated here, under the assumption the metastable states can be stabilized. For these estimates, the NASA-Lewis code[20] for prediction of rocket performance has been used to calculate specific impulse without extensive optimization.

H_3O

Results for various ratios of H_3O or D_3O and O_2 as well as for H_2 + 1/2 O_2 for comparison are shown in Table 2. A heat of formation of 12.458 kcal/mol for the lowest state of H_3O (or D_3O) was used in these calculations. This value was computed from our calculated relative energy with respect to H_2O + H and literature values[21] for the heat of formation of H_2O and H. The unstable energetic ion-pair state was not considered. Under the conditions considered thus far, H_2 + 1/2 O_2 is predicted to have an I_{sp} of 369 sec, whereas values greater than 400 sec are often quoted. D_3O, as a monopropellant, is predicted to be more favorable, with an I_{sp} of 396 sec. The lighter H_3O (which is, however, not predicted to be metastable), would still be more favorable, with a predicted value of 427 sec.

Table 2.

ESTIMATED I_{sp} FOR H_3O AND D_3O

	I_{sp}(s)
$H_2 + \frac{1}{2}O_2$	369.3
$H_3O + \frac{1}{2}O_2$	351.9
$H_3O + \frac{1}{3}O_2$	372.9
H_3O	427.0
$D_3O + \frac{1}{2}O_2$	337.3
$D_3O + \frac{1}{3}O_2$	354.9
D_3O	395.7

Li_3H AND RELATED COMPOUNDS

Using the calculated electronic energies, zero point energies, and literature values for the heats of formation[21] of LiH and Li_2, we calculate the heats of formation of the Li_3H $^1A'$ planar global minimum and ion-pair (pyramidal) configurations to be 51.06 and 71.36 kcal/mol, respectively. The heat of formation of the $^3A''$ state is predicted to be 69.62 kcal/mol. In Table 3, we list the specific impulse calculated with the NASA-Lewis code[20] for heats of formation approximating these values for combinations of Li_3H, O_2, and H_2. The H_2 was included following the suggestion of Rodgers,[22] who pointed out the improvement in predicted performance of H_2-O_2 with addition of Li. Ratios have been only approximately optimized.

Because the ground state of Li_3H lies more than 30 kcal/mol below LiH + Li_2, the molecule itself as a fuel, even if the triplet state or pyramidal form of the singlet can be used, is predicted to provide a low I_{sp}. However, Li_3H looks promising as an additive to H_2, with predicted I_{sp} values of 429 and 438 sec, respectively, for assumed heats of formation of 68 and 50 kcal/mol in the molar ratio Li_3H:H_2:O_2 of 5:30:4. Recall that under these conditions $H_2 + 1/2\ O_2$ has an I_{sp} of 369 s. Finally, from our calculated results we roughly estimate the heat of formation of Li_2H to be 50 kcal/mol. Use of Li_2H as an additive is estimated to be even more favorable, with a calculated specific impulse of 445 sec.

Table 3

ESTIMATED I_{sp} FOR Li COMPOUNDS

Molar Composition			I_{sp} (s)	
	H_2	O_2		
	2	1	369	
Li_3H	H_2	O_2	$\Delta H_f = 68$[a]	$\Delta H_f = 50$[a]
5	---	2	352	331
5	20	2	416	
5	30	4	438	429
Li_2H	H_2	O_2	$\Delta H_f = 50$[a]	
5	---	2	361	
5	30	4	445	

a. Energies in kcal/mol.

CONCLUSIONS AND IMPLICATIONS FOR FUTURE WORK

Several conclusions may be drawn from these studies of ion-pair states. First, in agreement with previous indications,[22] addition of compounds of Li is predicted to enhance performance of the H_2-O_2 system. Entrainment of atomic Li in hydrogen is made difficult by the tendency of Li to agglomerate to form the metal.[22,23] Introduction of Li in the form of Li_3H or Li_2H may ameliorate this problem. However, compounds of Li may also tend to form clusters; formation of oligomers of LiF,[24] for example, has been the subject of study. Thus, theoretical studies of dimer formation of these compounds and experimental investigation of stabilization, most probably in low-temperature matrices, appear to be valuable.

Second, from our work on H_3O and H_3F and the work of Michels[2,15] and Lester,[3] among others, on H_4 and H_3Li, the conclusion that charge separated species with H_3^+ as the positive ion are destabilized by back-charge transfer seems to be fairly well established. In proposing such species, the fact that covalent bonding often competes energetically with the ionic configuration should not be overlooked. This seems to be particularly troublesome for an open shell case, such as H_3O, in which a number of states arise from the same limits, but even H_3F, which has only one state arising from the ion-pair limit and no significant covalent bonding, does not have a stable ion-pair state. No further effort seems warranted on systems which include the H_3^+ moiety. However, it may be possible to exploit the large electron affinity of atomic fluorine and certain fluorine-containing compounds, (e.g., BeF_3, BF_4) by combining them with cations for which the corresponding neutrals have particularly small ionization potentials. This would minimize the back-charge transfer mechanism, which has limited the stability of many of the ion-pair systems studied to date.

PUBLICATIONS ATTRIBUTED TO THIS CONTRACT

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Appendix A

THEORETICAL STUDY OF LOW-LYING STATES OF H_3O

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Theoretical study of low-lying states of H_3O

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The first two doublet and quartet states of H_3O have been surveyed by multiconfiguration self-consistent field/first-order configuration interaction (MCSCF/FOCI) calculations in C_{3v} symmetry. Geometries of the minima on the doublet surfaces have been optimized by MCSCF gradient techniques and energies obtained by large-scale multireference single and double excitation CI calculations. The correlation diagram linking the minima to different dissociation limits has been established. A local minimum in C_{3v} symmetry of ion-pair character is shown to be unstable with respect to dissociation to $H_2 + H + O$. The lowest state, $1\,^2A_1$ in C_{3v}, ($1\,^2A'$ in C_s) may be characterized as an H_3O^+ core surrounded by an oxygen 3s Rydberg electron. Transition states for dissociation of the $1\,^2A'$ state to $H_2O + H$ and to $OH + H_2$ have been investigated. An extremely low barrier height, 3.58 kcal/mol without vibration, 0.4 kcal/mol for H_3O, an estimated 1.3 kcal/mol for D_3O, with zero-point energy, is found for dissociation of the $1\,^2A'$ state to $H_2O + H$. Within the uncertainty of the calculation it is not possible to predict whether the lowest state of H_3O should be observable experimentally. The relationship of these results to experimental observations for H_3O is discussed.

INTRODUCTION

There is considerable intrinsic interest in understanding novel bonding situations in polyatomic molecules. In addition, stable states of molecules with high energy content are of potential practical significance for the development of new propellants.[1] A recent model based on charge separation in an excited species has been proposed to predict the existence of stable excited states even in compounds with unstable ground states and has been applied to explain[2] a calculated local minimum in excited H_4. At the geometry of the minimum, the system may be described as H_3^+ in its equilateral triangle ground state with a H^- ion above the center of the triangle and, therefore, may be considered an ion-pair state. While subsequent calculations[3,4] have indicated the lowest state of H_4 can be expected to decay to $2\,H_2$, the class of ion-pair states of polyatomics remains of general interest and largely unexplored.

We have undertaken, therefore, a series of theoretical surveys of ion-pair and nearby states of small polyatomic molecules. In this paper, we report on our initial work on the H_3O system. Because the strength of the ion-pair bond is expected to be in some sense proportional to the stability of the negative ion and the oxygen atom has an electron affinity of 1.46 eV,[5] nearly twice that of atomic hydrogen, H_3O was selected as an interesting candidate system. Furthermore, there is substantial theoretical[6] and experimental[7-10] interest in the existence of stable or metastable H_3O, in its spectroscopy[11,12] as an example of a Rydberg molecule, and in the potential surface[13-16] for the hydrogen abstraction reaction $OH + H_2 \rightarrow H_2O + H$.

As reviewed in previous work,[6,7,9] the possible existence of the H_3O radical has been the subject of investigation for more than 20 years. Experimental evidence for metastable states of D_3O, but not of H_3O, has been reported by Gellene and Porter[7] from analysis of fast neutral beam scattering profiles and collisional reionization mass spectra. A subsequent paper by Raskit and Porter,[8] however, found no evidence of metastable $D_3{}^{18}O$. Griffiths *et al.*[9] have reported experimental evidence by neutralization–reionization spectroscopy of H_3O radicals with a lifetime of 0.41 μs. However, from an independent neutralization-reionization experiment, March and Young[10] have concluded that there is insufficient evidence to support the claim the H_3O radical survives for a transit time of 0.41 μs. The trace mass spectrometric signal at the mass-to-charge ratio of 19 appropriate for H_3O is identified as DHO^+.

The most recent theoretical study by Niblaeus, Roos, and Siegbahn (NRS)[6] found a local minimum on the lowest potential surface of H_3O in C_{3v} geometry 20.5 kcal/mol above $H_2O + H$ with a barrier to dissociation reported as 3.4 kcal/mol, which was expected to be too shallow to contain a vibrational level. Thus, the existence of metastable H_3O in the gas phase with a measurable lifetime was judged to be improbable.

The H_3O molecule is included in the recent discussion by Herzberg[11] of hypervalent hydrides which might be expected to exist as Rydberg molecules chiefly because of the stability of the corresponding ground state ion. However, in that review he reports that no discrete spectral features have been found and the broad continuous bands that were found are difficult or impossible to identify. The locations of Rydberg energy levels of H_3O have been predicted theoretically by Raynor and Herschbach[12] using a SCF and Koopmans' theorem approach.

Finally, the importance of the $OH + H_2$ reaction in hydrogen/oxygen flames has led to a number of studies[13-15] of the ground state potential surface, all of which lead to a planar transition state with a classical barrier height of ~ 6 kcal/mol. Although at nearly the same energy, this transition state is at a completely different geometry and has a completely different character than the minimum identified by Niblaeus, Roos, and Sieghbahn (NRS).[6] The long range part of the $OH-H_2$ potential has been considered by Ko-

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chanski and Flower[16] who were interested in rotational excitation of OH by H_2 at interstellar temperatures.

In this work, we have used a MCSCF/CI approach to survey the low-lying states of H_3O, paying particular attention to the symmetric geometries expected for $H_3^+ - O^-$ interaction. Local minima on the lowest two doublet surfaces of H_3O have been identified and characterized. The correlation diagram linking these minima to the different possible dissociation products has been established and the barriers to dissociation to $H_2O + H$ and to $OH + H_2$ have been determined by MCSCF gradient techniques. Computational issues addressed during the course of this study are also discussed.

CALCULATIONS

Two Gaussian basis sets have been used in our CASSCF/CI calculations of H_3O. The initial survey of the low-lying potential surfaces of H_3O used a double zeta plus polarization[17] basis set augmented by diffuse *s* (0.08) and *p* (0.06) functions on oxygen,[6] O(5s3p1d) H(2s1p), denoted DZPR. The diffuse functions have been added to describe the negative ion for those states that can be thought of as $H_3^+ + O^-$ or to describe Rydberg character. For the final calculations of the stationary points, the basis set denoted DZP2R included an additional diffuse *s*(0.03) and *p*(0.02) function on oxygen for more accurate description of the Rydberg states.

In the survey calculations, molecular orbitals optimized on the lowest state ($1\,^2A'$) were obtained by the complete active space (CAS) MCSCF procedure in which nine electrons were correlated in a seven orbital active space. Only the orbital arising from the oxygen 1*s* was kept frozen. Energies were obtained from first-order CI (FOCI) calculations that included all single excitations from the active space. Except as noted, calculations were carried out in C_s symmetry, in which the symmetry plane is perpendicular to the plane of the three H atoms and includes the O atom. In $^2A'$ symmetry, for example, the MCSCF expansion ($5a'$, $2a''$ active space) results in 250 configurations and the FOCI in 14 902 (17 080) configurations with the DZPR and DZP2R basis sets.

Geometries of the minima and transition states were optimized at the MCSCF level (DZP2R basis) using analytic second derivatives. At these points, energies were obtained by multireference single and double excitation CI (MRSDCI) calculations using MCSCF orbitals optimized on the lowest state of each molecular symmetry. Configurations which differed by at most two electrons from a set of 2–9 reference configurations were included in the CI expansions, which totaled ~25 000–118 000 configurations. The weight of the reference configurations in the resulting CI wave function was ~0.94–0.95 for all calculations.

As discussed below, at certain geometries, the second electronic state is a 3p Rydberg state, i.e., an H_3O^+ core surrounded by an oxygen 3*p* Rydberg electron. For CI calculations on this state in $^2A'$ symmetry, an O(3*p*) orbital determined as the virtual orbital of a SCF calculation on H_3O^+ was added to the active space, resulting in a (6,2) active space. The most similar orbital in the external space was deleted.

A limited number of calculations at the complete second-order CI (SOCI) level which included all single and double excitations from the active to the external space without limitation by reference configurations totalling ~330 000 configurations with the DZPR basis were also performed. These calculations and other technical problems addressed in the course of our study of H_3O are reported in a separate section below.

Some preliminary geometry optimizations were carried out with the GAMESS program[18]; final geometry determinations[19] and all other calculations used the ALCHEMY II program system.[20]

POTENTIAL SURFACES AND MINIMA

Survey of C_{3v} geometries

We first present a survey of potential surfaces of H_3O calculated with the DZPR basis set and restricted to C_{3v} symmetry. This restriction is consistent with our model of the ion pair as a H_3^+ ion and is also consistent with the symmetric pyramidal geometry optimized by NRS[6] for the lowest state. The geometries have been characterized in terms of two parameters: *a*, the H–H distance, i.e., the side of the hydrogen equilateral triangle, and *d*, the vertical distance from the oxygen atom to the center of the triangle. The lowest state belongs to the totally symmetric $^2A_1$ symmetry in C_{3v} ($^2A'$ in C_s) symmetry. The second state is a doubly degenerate ^2E state in C_{3v}, which has two components, the $2\,^2A'$ and $1\,^2A''$ states in C_s symmetry.

Results for the lowest potential energy surface of H_3O at various fixed H–H distances between 1.65 and 3.50 a_0 are shown in Fig. 1 as a function of the vertical oxygen distance. At H–H distances near 1.65 a_0, the equilibrium separation of H_3^+, the wave function is a $H_3^+ - O^-$ ion pair as anticipated. However the lowest energy is found for a much larger H–H distance and closer approach by oxygen, i.e., $a = 3.05\ a_0$ and $d = 0.92\ a_0$, where the system can be described as a H_3O^+ ion with a Rydberg *s* electron on oxygen. This is in qualitative agreement with the results of the previous study by NRS.

Cuts through the potential surface at constant H–H distance for the $1\,^2E$ excited state are shown in Fig. 2. The required equivalence between the $2\,^2A'$ and the $1\,^2A''$ states was confirmed in our calculations in C_s symmetry. There are two distinct minima in the $1\,^2E$ state in C_{3v} geometries and there is no path without an energy barrier for conversion of the upper local minimum to the lower one in symmetric geometries. The upper minimum occurs at a H–H separation of 1.65 a_0. At this geometry, which corresponds to the equilibrium geometry of H_3^+, on the basis of population analysis of the natural orbitals, both the first and second ^2A states can be identified as true ion pairs. (Because of the open shell nature of O^-, $1s^2 2s^2 2p^5$, combinations of H_3^+ and O^- can lead to more than one state.) In these calculations, with the DZPR basis set, at the geometry of the lower minimum, the $2\,^2A'$ state is a valence state. However, as reported below, when provision is made to treat the 3*p* Rydberg state proper-

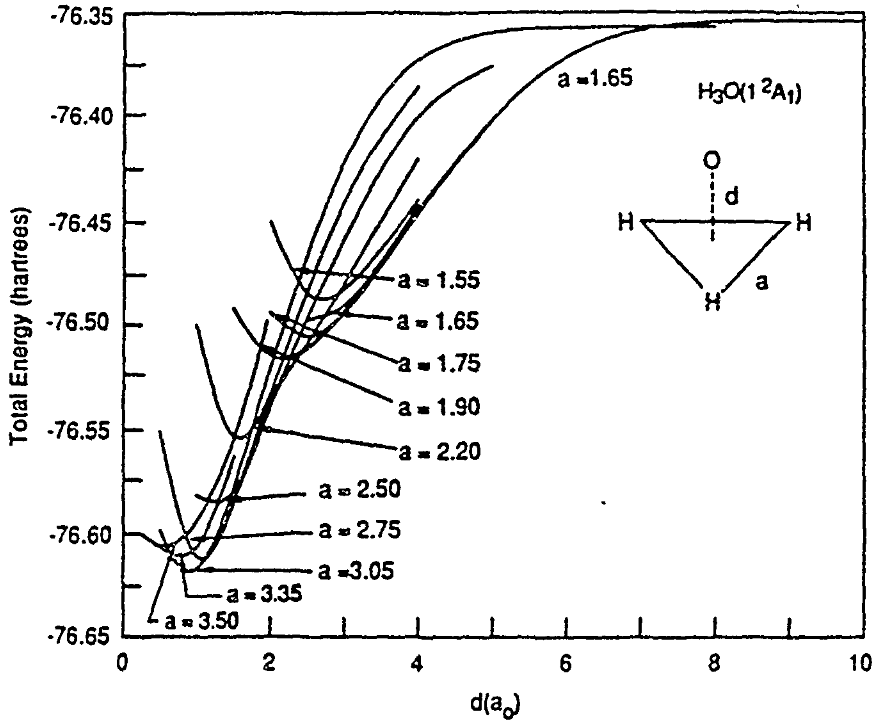

FIG. 1. Cuts through the $1\,^2A_1$ in C_{3v} symmetry, ($1\,^2A'$ in C_s) potential surface at fixed H–H distance a, as a function of the distance of the O from the H_3 plane d, calculated at the FOCI level (DZPR basis set).

ly, our final calculations indicate the $3p$ Rydberg state is lower in energy than this valence minimum.

The potential energy surfaces for the corresponding states of quartet symmetry have also been investigated and are illustrated in Fig. 3. As for the doublet states, the lowest state is the $1\,^4A_1$ and the second state is the $1\,^4E$, corresponding to the $2\,^4A'$; and $1\,^4A''$ states in C_s symmetry. There is no binding in states of quartet multiplicity in C_{3v} geometries. These states have not been considered further in this study.

Optimized geometries

From this survey, there are three local minima in C_{3v} restricted geometries to be characterized: the lowest point on the $1\,^2A_1$ ($1\,^2A'$) surface and the two local minima on the $1\,^2E$ ($2\,^2A'$, $1\,^2A''$) surface. When the C_{3v} symmetry is relaxed, of course, the $1\,^2A''$ and $2\,^2A'$ surfaces are no longer degenerate. Optimized geometries in lower symmetry are summarized in Table I and illustrated in Fig. 4.

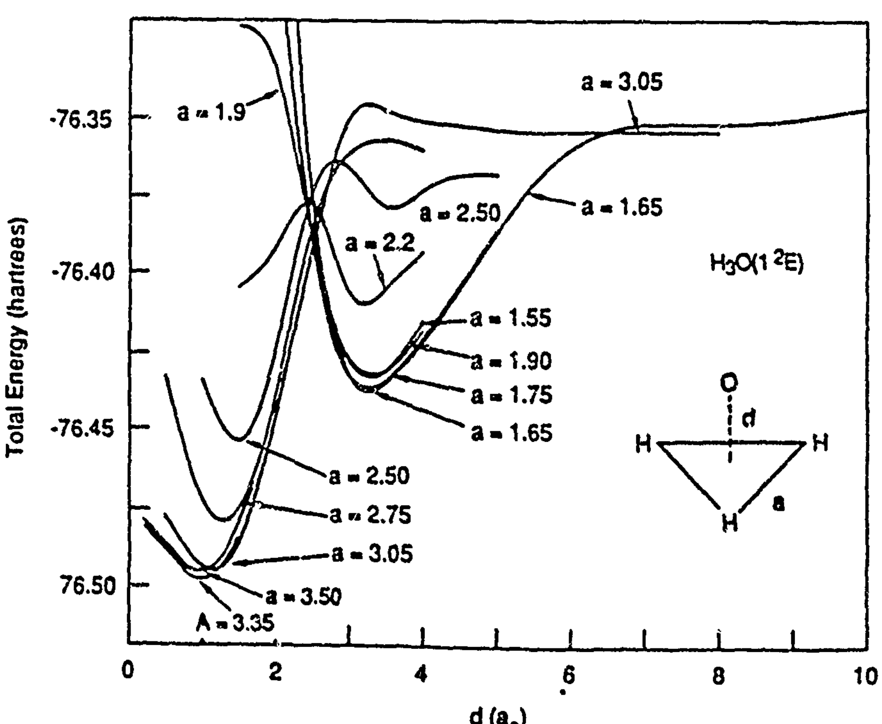

FIG. 2. Cuts through the $1\,^2E$ in C_{3v} symmetry, ($2\,^2A'$, $1\,^2A''$ in C_s) potential surface at fixed H–H distance a, as a function of the distance of the O from the H_3 plane d, calculated at the FOCI level (DZPR basis set).

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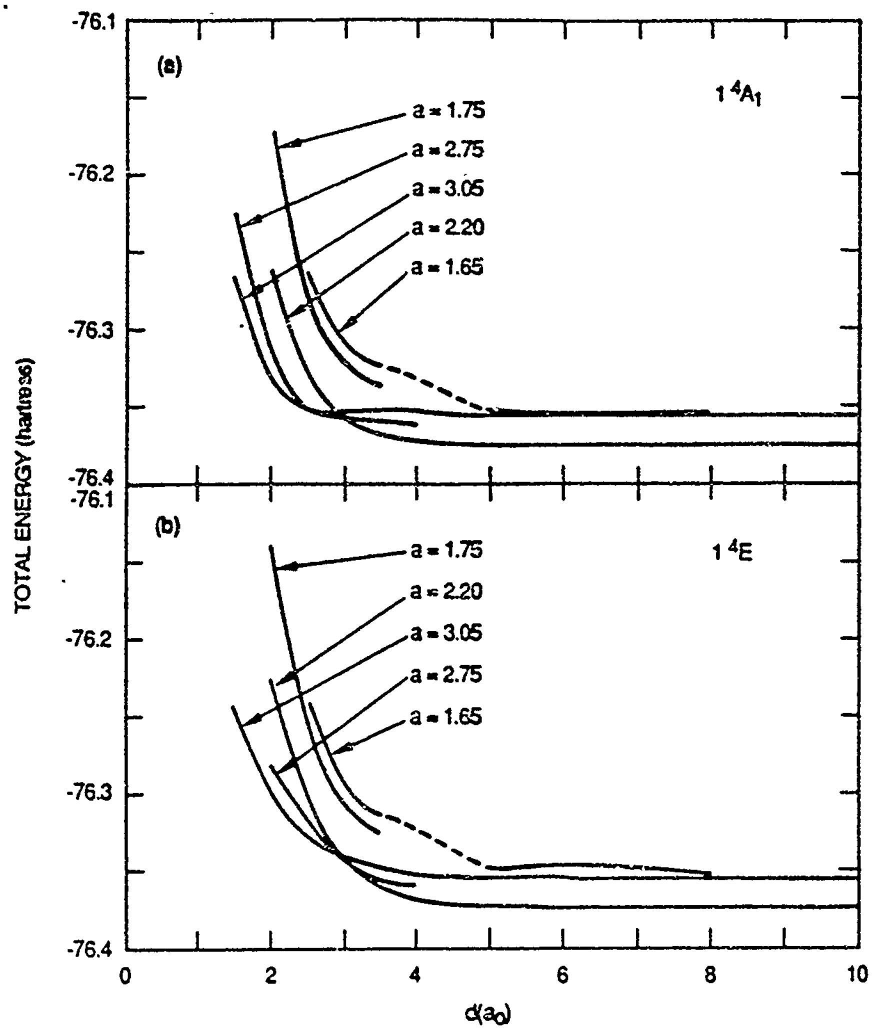

FIG. 3. Cuts through the (a) $1\,^4A_1$, (b) $1\,^4E$ potential surfaces at fixed H–H distance a, as a function of the distance of the O from the H_3 plane d, calculated at the FOCI level (DZPR basis set). Dashed line indicates gap between calculations started from small and large distance d. (See the text).

As determined by MCSCF analytic second derivative optimization with the DZP2R basis set, the true minimum (all real frequencies) on the $1\,^2A'$ surface has C_{3v} symmetry. The MCSCF optimized geometry of the $1\,^2A'$ state obtained in this work is in good agreement with the unrestricted Hartree-Fock (UHF) optimized geometry of NRS as expressed in Table II in terms of the OH bond length, 1.012 Å in the present work vs 0.989 Å, NRS, and the HOH bond angle. The slightly smaller bond angle, 105.1, present work, vs 109.5, NRS, corresponds to slightly larger vertical distance (0.404 vs 0.330 Å) between the oxygen and the plane of the three hydrogens. The HH distances are extremely close in the two optimizations. At the MCSCF level, the difference in energy between the present structure and that of NRS is 1 kcal/mol. Because the $1\,^2A'$ state is a Rydberg state, it is expected to have a very similar geometry to the H_3O^+ ion,[21,22] which is also demonstrated in Table II.

MCSCF gradient optimization predicts two minima (with six re' frequencies) on the $1\,^2A''$ potential surface. The lowest i. nergy is a $3p$ Rydberg state and is very similar in geometry to the $1\,^2A'$ state, the $3s$ Rydberg state. Optimization of the $^2A''$ state in C_s symmetry will inevitably break the C_{3v} symmetry. The geometry difference is not significant, the illustrations could not be distinguished in Fig. 4. At the higher minimum, which is quite distorted from C_{3v} symmetry, the $^2A''$ state is a valence state. Finally, the optimized geometry of the ion-pair minimum on the $1\,^2E$ potential surface, the upper minimum in Fig. 2, has been determined within C_{3v} symmetry by variation of the parameters a and d. However, the ion-pair state is not stable w.h respect to distortion from C_{3v} symmetry as reported below

Energies

Total energies for the optimized minima from MRSDCI calculations (DZP2R basis set) are also listed in Table I Relative energies are given with respect to the $H_2O + H$ asymptote. The $1\,^2A'$ state, the $3s$ Rydberg state, is predicted to lie 17.93 kcal/mol above $H_2O + H$, in reasonable agreement with the 20.5 kcal/mol value obtained previously[6] At this geometry the $^2A'$ symmetry MRSDCI calculation was carried out with the larger active space to treat the $3p$ Rydberg state. From analysis of the natural orbitals and the CI coefficients, the $2\,^2A'$ state may be characterized as a $3p$ Rydberg state with, however, some admixture of valence character. In calculations on the isoelectronic system, FH_2, Petsalakis *et al.*[23] found the first excited state, the $1\,^2B_2$, to have a mixed Rydberg and valence antibonding character The rel

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TABLE I. Optimized geometries (a_0), total energies, zero-point energies, and relative energies for minima on first two doublet surfaces of H_3O.

State	Symmetry	Geometry	Total energy (hartrees) MCSCF	Total energy (hartrees) MRSDCI	Relative energy[a] (kcal/mol)	Zero-pt Energy (kcal/mol)	Relative energy[a] with zero pt (kcal/mol)
$1\,^2A_1\,(1\,^2A')$	$C_{3v}(C_s)$	O–H 1.912 H–H 3.036 d 0.764	−76.556 186	−76.727 647	17.93	18.08	23.14
$1\,^2E(2\,^2A',1\,^2A'')$	$C_{3v}(C_s)$	O–H 1.912 H–H 3.036 d 0.764		−76.641 597	71.94		
$1\,^2A''$ (3p Rydberg)	C_s	O–H1 1.864 O–H2 1.877 H1–H2 3.007 H2–H3 3.110	−76.479 853	−76.638 687	73.77	23.49	84.39
$1\,^2A''$ valence	C_s	O–H1 1.850 O–H2 2.462 H1–H2 3.291 H2–H3 3.465	−76.465 506	−76.627 716	80.65	17.36	85.14
$1\,^2E(2\,^2A',1\,^2A'')$ (ion pair)	C_{3v}	O–H 3.627 H–H 1.650 d 3.5	−76.349 011	−76.531 298[b]	141.57[b]		

[a] With respect to $H_2O + H$ MCSCF −76.603 067 MRSDCI −76.756 204.

[b] SOCI/DZPR $H_2O + H$ asymptote = −76.756 837.

ative energy of the $3p$ state of H_3O is 71.94 or 54.0 kcal/mol above the $3s$ Rydberg state. Note that essentially the same prediction, a relative energy of 73.77 kcal/mol is given for the $3p$ Rydberg state by MRSDCI calculation on the $^2A''$ symmetry with the (5,2) active space at the geometry obtained by $^2A''$ MCSCF optimization.

The non-Rydberg minimum on the $1\,^2A''$ potential surface is somewhat higher at 80.65 kcal/mol. Finally, the ion-pair local minimum on the $1\,^2E$ surface is much higher in energy, 141.57 kcal/mol. This energy was obtained from a second-order CI calculation with the DZPR basis set, which, as shown below, should be entirely consistent with the other energies.

CORRELATION DIAGRAM

The correlation diagram connecting the $1\,^2A_1$ and $1\,^2E$ states of H_3O and the corresponding states in C_s symmetry to the states of the possible dissociation limits, $OH + H_2$, $H_2O + H$, $H_3 + O$, $H_3^+ + O^-$, and $O + H + H_2$, based only on symmetry considerations is shown in Fig. 5. Energies of the asymptotes with respect to $H_2O + H$, excluding zero point energy, summarized in Table III, have been obtained as follows: The experimental heats of formation,[24] modified by the experimental zero point energies[25,26] are taken for the $OH(X\,^2\Pi) + H_2$ and the $H_2 + H + O$ asymptotes. Spectroscopic T_e values have been used for the excited states of OH and H_2O. The ground state surface of H_3 is repulsive with respect to $H_2 + H$. The $H_3 + O$ asymptote has been placed according to the second order CI calculated energy difference between H at the H_3^+ equilibrium geometry, $a = 1.65\,a_0$, and that of $H_2 + H$. Finally, the accurate calculated value for the H_3^+ dissociation energy[7] and the experimental oxygen electron affinity[5] have been taken for the ion-pair limit. The correlations drawn for the $1\,^2E$ state on the basis of symmetry apply as well to the ion-pair minimum (not shown) which lies ~70 kcal/mol higher in energy.

The $H_3 + O$ and $H_3^+ + O^-$ limits, which are very high in energy, each give rise to an A_1 and E state and thus correlate in C_{3v} symmetry to the lowest states of H_3O. Of greater interest are the correlations to the $H_2O + H$ and $OH + H_2$ asymptotes which have been drawn in C_s symmetry. Using the C_s state designations, the $1\,^2A'$ state correlates with the ground state of $OH + H_2$ and of $H_2O + H$ and is higher in energy than either of these limits. The $2\,^2A'$ state is bound with respect to the excited states of OH and H_2O, with which it correlates. The $1\,^2A''$ state, however, correlates to the OH ground state, which has both an A' and A'' component. In the other direction, the $1\,^2A''$ state correlates to a highly excited state of $H_2O + H$. Coupling between the $1\,^2A''$ and $2\,^2A'$ states would cause the stability of the $2\,^2A'$ state to depend on that of the $1\,^2A''$ state. Anticipating our results for the ion-pair local minimum, we also note that the $1\,^2E$, state correlates to the $H_2 + H + O$ limit in C_1 (no) symmetry.

From this correlation diagram, barriers in the dissocia-

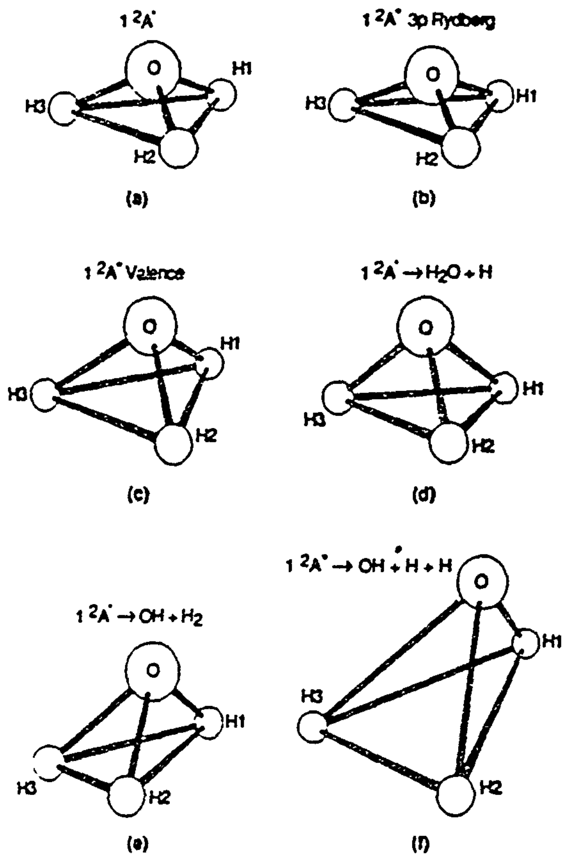

FIG 4. Geometries optimized by MCSCF gradient calculations (DZP2R basis) (a) $1\,^2A'$ minimum, (b) $1\,^2A''$ 3p Rydberg minimum, (c) $1\,^2A''$ minimum of valence character, (d) transition state $1\,^2A' \rightarrow H_2O + H$, (e) Stationary point with two imaginary frequencies determined in search for transition state $1\,^2A' \rightarrow OH + H_2$ (see the text), and (f) transition state $1\,^2A''$ valence minimum $\rightarrow OH + H + H$.

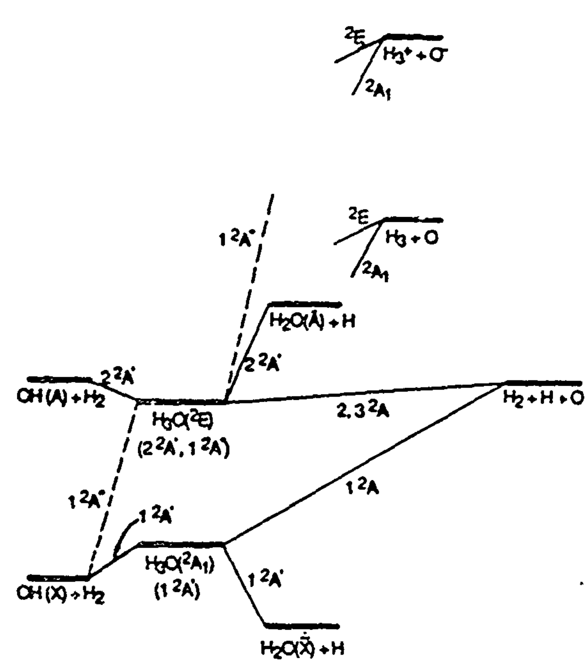

FIG. 5. Correlation diagram linking the $1\,^2A_1$ and the $1\,^2E$ states of H_3O to asymptotic limits on the basis of symmetry. The $H_3^+ + O^-$ and $H_3 + O$ limits have been connected in C_{3v} symmetry, the $OH + H_2$ and $H_2O + H$ limits have been connected in C_s symmetry and the $H_2 + H + O$ limit in C_1 (no) symmetry.

tion of the $1\,^2A'$ state to $H_2O + H$ and to $OH + H_2$ and of the $1\,^2A''$ state to $OH + H_2$ need to be determined. For the $1\,^2A''$ state, the relationship between the 3p Rydberg minimum and the valence minimum also needs to be investigated.

STABILITY OF POTENTIAL MINIMA: DISSOCIATION BARRIERS AND RADIATIVE LIFETIMES

Dissociation of the $1\,^2A'$ state

The transition states for dissociation of the minimum on the lowest potential energy surface to $H_2O + H$ and to $OH + H_2$ have been investigated by MCSCF gradient optimization. Geometries, energies, and zero point energies (5 or 4 real frequencies) of the stationary points are listed in Table IV. A very low barrier, 3.58 kcal/mol, is found for dissociation to $H_2O + H$, which has a conventional transition state with one imaginary frequency (2310i). The geometry of the transition state is in between that of the $1\,^2A'$ minimum and of H_2O. The symmetric hydrogens, H2 and H3 in Fig. 4, form the H_2O molecule. Including the zero-point energy which is larger by 3.2 kcal/mol for the $1\,^2A$ equilibrium than for the transition state, the barrier height is reduced to 0.40 kcal/mol. This value is smaller than uncertainties in the calculation. Note that the transition state ge-

TABLE II. Comparison of H_3O $1\,^2A'$ and H_3O^+ geometry (bond length in Å, angles in degrees) and zero-point energy (kcal/mol).

	$H_3O(1\,^2A')$		H_3O^+	
	Present work	Ref. 6[a]	Calculated[b]	Expt[c]
O–H	1.012	0.989	0.987	
∠HOH	105.1	109.5	111.6	111.3
Zero-point energy	18.08		20.52	

[a] UHF optimization.
[b] DeFrees and McLean, Ref. 21, 6-31G* basis CI opt.
[c] Symons, Ref. 22 deduced from nuclear magnetic resonance (NMR) data.

TABLE III. Energies of asymptotes in kcal/mol relative to $H_2O + H$ excluding zero-point energy.

Asymptote	Relative energy
$H_2O\,(\tilde{X}\,^1A_1) + H$	0.0
$H_2O\,(\tilde{A}\,^1B_1) + H$	153.71[a]
$OH\,(X\,^2\Pi) + H_2$	16.0[b]
$OH\,(A\,^2\Sigma^+) + H_2$	109.48[c]
$H_2 + H + O$	122.67[b]
$H_3 + O$	204.57[d]
$H_3^+ + O^-$	296.30[e]

[a] Herzberg (Ref. 26).
[b] Heats of formation (Ref. 24) modified by zero point energies (Refs. 25 and 26).
[c] Huber and Herzberg (Ref. 25).
[d] Calculated (present work).
[e] H_3^+ dissociation energy Dykstra *et al.* (Ref. 27), O electron affinity (Ref. 5).

TABLE IV Optimized geometries (a_0), total energies, zero-point energies, and relative energies for transition states and stationary points.

Transition	Geometry	Total energy (hartrees) MCSCF	Total energy (hartrees) MRSDCI	Relative energy[a] (kcal/mol)	Zero-pt energy (kcal/mol)	Barrier height (kcal/mol)	Barrier height w/zero pt
$^2A'$ – H_2O + H	O–H1 2.209[b] O–H2 1.877 H1–H2 3.245 H2–H3 2.969	−76.552 494	−76.721 953	21.50	14.90	3 58	0.40
1 $^2A''$ – OH + H + H	O–H1 1.855 O–H2 4.241 H1–H2 4.675 H2–H3 4.014	−76.434 859	−76.572 264	115.46	10.65	34.81	28.09
1 $^2A''$ Rydberg → 1 $^2A''$ valence	O–H1 1.844 O–H2 2.198 H1–H2 3.153 H2–H3 3.264	−76.463 780	−76 632 432	77 69	16.79		
Stationary point[c]	O–H1 1.865 O–H2 2.373 H1–H2 3.247 H2–H3 2.131	−76.515 968	−76.687 349	43.22	11 38	25.30	18 60

[a] With respect to H_2O + H MCSCF −76.603 067 MRSDCI −76.756 204.
[b] NRS (Ref. 6) geometry O–H1 = 2.350, O–H2 = 1.821, H1–H2 = 3.422, H2–H3 = 2.943.
[c] Stationary point with two imaginary frequencies located in search for transition state 1 $^2A'$ – OH + H_2 (see the text).

ometry is quite similar to that found by NRS who reported a barrier height of 3.4 kcal/mol without zero-point energy, in excellent agreement with present results. We also find, in agreement with NRS, that the change from Rydberg to valence character as the 1 $^2A'$ state dissociates is due to a change in the molecular orbital and not to configuration mixing, an example of Mulliken's "MO Rydbergization."[28] A similar situation has been discussed in the dissociation of NH_4 to NH_3 + H.[29]

We were not successful in locating the transition state for dissociation of the 1 $^2A'$ state to OH + H_2. The stationary point characterized by two imaginary frequencies, 3493i and 1520i, that has been determined is reported in Table IV. In our search for the transition state, the stationary point geometry was distorted by varying amounts according to the normal modes associated with each imaginary frequency, in turn, to provide a starting point for further optimization. We found, however, that distortion of the transition state geometry in one direction according to the normal mode corresponding to the smaller frequency, which preserves C_s symmetry, led to optimization to OH + H_2, and distortion in the other direction led back to the 1 $^2A'$ minimum. Distortion of the transition state according to the normal mode of the larger imaginary frequency, which breaks C_s symmetry, led to formation of H_2O + H with one of the symmetric hydrogens becoming the hydrogen atom asymptotically. Distortion in the opposite direction led to elimination of the other symmetric hydrogen. The energy of the stationary point is 25.30 kcal/mol above that of the 1 $^2A'$ minimum. Stability of the 1 $^2A'$ state depends, in any event, on the very low barrier to formation of H_2O + H.

Dissociation of the 1 $^2A''$ state

The dissociation path of the lowest potential surface of $^2A''$ symmetry is more complicated. As shown in Table IV, two transition states have been identified at the MCSCF level. The one listed at the bottom of Table IV connects the Rydberg and valence minima on the 1 $^2A''$ surface. The geometry is in between that of the two minima. It has an imaginary frequency of 1672i and distortion of the transition state geometry in the two directions according to the imaginary mode leads to the two minima. The transition state lies approximately 1 kcal/mol above the 1 $^2A''$ valence minimum at the MCSCF level. However, MRSDCI calculations place the transition state 2.96 kcal/mol below the energy of the valence minimum. Thus, the true status of the valence minimum as a stationary point on the 1 $^2A''$ potential surface is in doubt.

The other transition state on the $^2A''$ surface lies at rather high energy, ~35 kcal/mol above the valence minimum. The transition state has a single imaginary frequency, 1854i. However, at the transition state geometry, the H_2 internuclear separation is extremely large, 4.0 a_0, and the MCSCF energy is within 1 kcal/mol of that of OH + H + H with OH at its equilibrium internuclear separation. Thus, it appears that the transition state that has been identified leads to OH + H + H and not to OH($X\,^2\Pi$) + H_2 as anticipated from the correlation diagram in Fig. 5. Distortion according

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to the imaginary mode in the other direction definitely leads back to the $1\,^2A''$ valence minimum. It was not possible to locate a transition state with smaller H–H distance within C_s symmetry.

From these results, it is not possible to unambiguously describe the dissociation of the $1\,^2A''$ state. Further exploration at the CI level would be required to determine if a valence minimum exists. More imporantly, investigation in lower symmetry would be required to search for a lower energy path to $OH(X^2\Pi) + H_2$

Dissociation of the ion-pair minimum

The ion-pair minimum on the $1\,^2E$ potential energy surface lies higher in energy than the $H_2 + H + O$ asymptote and is connected to it by symmetry. The plot in Fig. 6 demonstrates that distortion of the C_{3v} geometry of this local minimum leads to dissociation of the $2\,^2A'$ state (2^2A in C_1 symmetry) to $H_2 + H + O$ without a barrier. The dissociation path chosen is as follows. FOCI energies obtained with the DZPR basis set have been plotted. Starting from the equilibrium geometry, $a = 1.65\ a_0$, $d = 3.5\ a_0$ and keeping the vertical distance, d, and the two sides of the triangle constant, the triangle has been opened gradually with a base going from 1.65 to 3.30 a_0 where the three H's are aligned and kept equidistant from the central H. Then one of the H's and the O were gradually pulled out while the two remaining hydrogens were moved closer until the equilibrium geometry of H_2 (1.402 a_0) was attained. The reaction coordinate reported in Fig. 6 is the distance between the two most distant hydrogens. While this may not necessarily provide the minimum energy path, it is sufficient to establish that the ion-pair state of H_3O is not expected to be stable.

The $3\,^2A$ state ($1\,^2A''$ in C_s symmetry), also plotted in Fig. 6, shows a barrier on the chosen dissociation path due to an interaction with a higher ion-pair state. We have not optimized the path for this state because, in any event, coupling with the $^2A'$ state should prevent stability of the $^2A''$ component of the ion-pair minimum.

Radiative lifetimes

Transition dipole matrix elements connecting the $2\,^2A'$ and the $1\,^2A''$ states with the $1\,^2A'$ state have been calculated from FOCI wave functions at the geometries of the upper state minima and used to estimate oscillator strengths and radiative lifetimes, listed in Table V, from the very approximate formulas given there. The $3p$ Rydberg state has an estimated lifetime of 18 ns which corresponds to a transition probability of $5.46\times 10^7\ s^{-1}$. Raynor *et al.*[12] obtained a transition probability of 5.64×10^7 for this state. Note that essentially the same result is obtained for the $3p$ state whether calculated in $^2A'$ or $^2A''$ symmetry. At the geometry of the $1^2A''$ valence minimum, the calculated transition moment is approximately half as large which would correspond to a radiative lifetime of 34 ns if the upper state is considered as a bound state.

COMPUTATIONAL ISSUES

Although the final energies at the stationary points were determined by MRSDCI calculations, a great deal of exploration was performed at the FOCI level. The comparisons of total and relative energies at the $1\,^2A'$ equilibrium geometry and at the $H_2O + H$ and $OH + H_2$ asymptotes at their spectroscopic geometries reported in Table VI provide the calibration of FOCI results.

The most important comparison is that between the

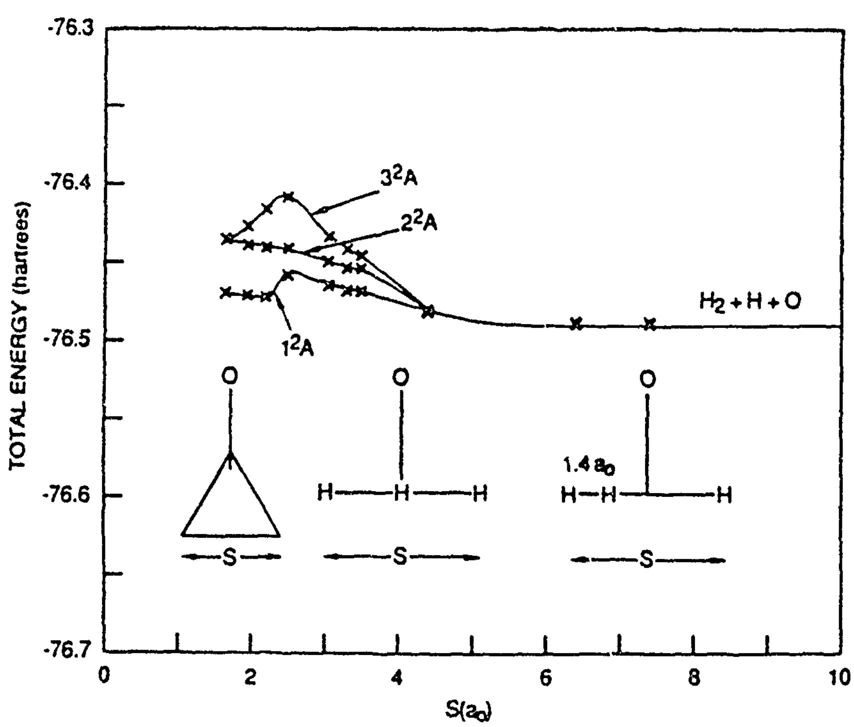

FIG. 6. Dissociation of the upper local minimum on the $1\,^2E$ potential surface of H_3O to $H_2 + H + O$ as a function of the pseudo reaction coordinate S defined in the figure, calculated at the FOCI level (DZPR basis set).

TABLE V. Transition dipole matrix elements, oscillator strengths and estimated lifetimes for $2\,^2A'$ and $1\,^2A''$ states of H_3O.

Transition	Geometry	$\sqrt{\Sigma_i \langle r_i \rangle^2}$	λ(Å)[a]	f[b]	τ(ns)[c]
$2\,^2A' \to 1\,^2A'$	$1\,^2A'$ min	2.311	5824	0.278	18
$1\,^2A'' \to 1\,^2A'$	$1\,^2A''$ $3p$ Rydberg	2.415	5805	0.305	17
$1\,^2A'' \to 1\,^2A'$	$1\,^2A''$ valence	1.112	4382	0.086	34

[a] Calculated from electronic energy difference.
[b] Estimated as $f = \frac{2}{3}\Delta E\,(\Sigma_i \langle r_i \rangle^2)$.
[c] Given by $\tau^{-1}\,(s^{-1}) = A = [f/\lambda^2(\text{Å})]\; 6.670\,246 \times 10^{15}$.

(6,2)FOCI and the (6,2)MRSDCI at the $1\,^2A'$ minimum, both of which have a larger active space to accomodate the $3p$ Rydberg orbital. The relative energy of the $1\,^2A'$ state with respect to $H_2O + H$ changes by less than 0.2 kcal/mol on inclusion of double excitations in the CI expansion, while the difference in relative energy of the $2\,^2A'$ state, the $3p$ Rydberg state, is 4 kcal/mol. The CI coefficients and natural orbitals were extremely similar in the two calculations. Thus, the FOCI provides meaningful results for the H_3O molecule. Comparing the (5,2) and (6,2) FOCI results, we observe that, as expected, the total energy of the $1\,^2A'$ state is virtually unaffected by the inclusion of the $3p$ orbital.

The transition dipole moment connecting the $1\,^2A'$ and $2\,^2A'$ states is unaffected by the double excitations. A value of 2.311 ea_0 is obtained from FOCI calculation as compared with 2.315 ea_0 from the MRSDCI. Therefore, transition dipole moments from FOCI calculations with a common orbital set ($^2A'$ MCSCF orbitals) were reported in Table V. For calculation of the $3p$ Rydberg state in $^2A''$ symmetry, an a'' symmetry $3p$ SCF virtual orbital was added to the active space, resulting in a ($5a'$, $3a''$) active space.

A few additional comparisons are also noted in Table VI. Limiting the FOCI expansion to at most double excitations with respect to the same set of reference configurations, labeled FOCI (refs), is seen to have a negligible effect, as compared with the full FOCI. This limitation was imposed in the MRSDCI calculation. At the asymptotes, the MRSDCI result is compared with a complete second order CI calculation (SOCI), which includes all single and double excitations from the active space to the internal space without restriction by reference configurations. Introduction of reference configurations modifies the total energy by 0.6 mhartrees and the relative energy of the asymptotes by <0.1kcal/mol. The effect of selecting reference configurations has recently been discussed by Taylor and Partridge.[30] The SOCI calculation was done with the smaller DZPR basis set. The comparison, however, is valid because at the asymptote, use of the DZP2R basis set changes the MCSCF and FOCI energies by <0.2 mhartrees.

The $OH + H_2$ excitation energy with respect to $H_2O + H$ is calculated at the FOCI level to be 16.13 kcal/mol, in fortuitously close agreement with the experimental result of 16.0 kcal/mol, determined by modifying the experimental heat of formation by the zero-point energies. Introduction of double excitations reduces the relative energy by 4.7 kcal/mol. The FOCI result is consistent with the results of Walch and Dunning[13] who obtained 16.7 kcal/mol with a

TABLE VI. Comparison of calculation at $1\,^2A'$ minimum and at $H_2O + H$ and $OH + H_2$ asymptotes.

	$1\,^2A'$[a]		$2\,^2A'$[a]	
	Total energy (hartrees)	Relative energy[b] (kcal/mol)	Total energy (hartrees)	Relative energy[c] (kcal/mol)
(5,2) FOCI	−0.634 937	18.77		
(6 2) FOCI	−0.636 162	18.01	−0.556 704	49.87
(6,2) FOCI (refs)	−0.635 915	18.10	−0.556 224	50 03
(6,2) MRSDCI	−0.727 647	17 93	−0.641 597	54 01
(6,2) FOCI/(6,2) orbitals	−0.654 706	20.51		

	$H_2O + H$[d] Total energy (hartrees)	$OH + H_2$[e] Total energy (hartrees)	$OH + H_2$[e] Relative energy[b] (kcal/mol)
(5,2) FOCI	−0.664 851	−0.639 148	16.13
(5,2) FOCI (refs)	−0.664 765	−0.639 098	16.11
(5,2) MRSDCI	−0.756 204	−0.738 047	11.40
(5,2) SOCI/DZPR	−0.756 837	−0.738 573	11.46
(6,2) FOCI/(6,2) orbitals	−0.687 379		
Expt			16.0

[a] $1\,^2A'$ minimum geometry.
[b] With respect to $H_2O + H$.
[c] With respect to $1\,^2A'$.
[d] H_2O geometry: OH = 1.810 a_0 $\theta = 104.5$.
[e] $r(OH) = 1.833\ a_0$ $r(HH) = 1.402\ a_0$.

comparable calculation (POL-CI) and comparable size basis set. Unpublished results of Kraka and Dunning[14] indicate a larger basis set, at least triple zeta + polarization is needed to obtain an excitation energy within 1 kcal/mol of experiment when double excitations are included in the wave function.

All of our calculations use MCSCF orbitals obtained with a (5,2) active space. Because, the 1 $^2A'$ minimum is a 3*s* Rydberg state, at this geometry, the complete active space should actually include an additional orbital (6,2) to accomodate the Rydberg orbital. At the asymptote or at any valence geometry, the larger active space would contain an "extra" orbital. This is a persistent problem in the MCSCF/CI treatment of Rydberg states. The relative energy of the 1 $^2A'$ 3*s* state with respect to the $H_2O + H$ asymptote has been determined by a (6,2) FOCI using MCSCF orbitals determined with the (6,2) active space. As shown in Table VI, use of the larger active space changes the excitation energy by only 2.5 kcal/mol. A previous study[31] of NH_2 demonstrated that use of a larger active space produces a tolerable variation in the interaction energy of valence geometries, even at the MCSCF level. We may also note the 3*s* Rydberg orbital from the larger MCSCF is very similar to that obtained from the (5,2) calculation. The additional orbital in the (6,2) MCSCF is the expected antibonding combination of the oxygen *p* and the H's to complete the active space.

The FOCI prediction illustrated in Fig. 6 that the ion-pair state dissociates without a barrier to $H_2 + H + O$ needs to be critically examined because the FOCI wave function does not give the correct sign for the electron affinity of the isolated oxygen atom. At the SOCI level, the electron affinity of oxygen is 0.82 eV with the DZPR basis and 0.84 eV with the DZP2R basis in qualitative agreement with the reported value,[5] 1.46 eV. The discrepancy with experiment is, however, small compared with the 7.77 eV coulombic attraction at the 2 $^2A'$ ion-pair local minimum.

In Table VII, the relative energy of the 2 $^2A'$ state calculated at the FOCI and SOCI level (DZPR basis) is compared at the ion-pair minimum and at two critical points along the dissociation path in Fig. 6. Truncating the CI expansion causes a maximum discrepancy of 2.3 kcal/mol in the 2 $^2A'$ state confirming the qualitative conclusion that the ion-pair local minimum dissociates without a barrier. We note that accurate calculation of the electron affinity of the oxygen atom remains a classic problem[32] in quantum chemistry requiring very extended basis sets and extensive treatment of correlation. Recent studies have used *f* functions[33] and *f*, *g*, and *h* functions![34] Such extensions are beyond the scope of the present study.

TABLE VII. Relative energy (kcal/mol) of 2 ^2A state with respect to $H_2O + H$.

	FOCI		SOCI
H2–H3 (a_0)[d]	DZP2R[a]	DZPR[b]	DZPR[c]
1.65	143.53	143.90	141.57
2.50		138.54	137.83
3.50		133.37	133.99

[a] $H_2O + H$ energy: − 76.664 851 hartrees.
[b] $H_2O + H$ energy: − 76.664 667 hartrees.
[c] $H_2O + H$ energy: − 76.756 837 hartrees.
[d] Corresponds to coordinate *S* in Fig. 6.

Finally, we note that it was necessary to monitor the MCSCF wave function when approaching dissociation limits from smaller internuclear separations, i.e., from the left in Figs. 1–3 and 6. Particular difficulties were observed in the original survey calculations at large H_3–O distances. The wave function remained an ion-pair instead of attaining the neutral $H_3 + O$ asymptote, which is lower in energy. In mapping the ion-pair dissociation, Fig. 6, the H_3 antibonding orbital, which should become an H_2 antibonding orbital at the $H_2 + H + O$ asymptote, became instead an oxygen 2*p* correlating orbital. To overcome these difficulties, the calculations were started at long range from localized orbitals and carried inward until the results matched those started from short range calculations. The small region not covered in some of our calculations on the quartets is indicated by a dashed line in Fig. 3.

DISCUSSION

Ion-pair states

While one of the motivations for this work was to investigate a possible energetic ion-pair state of H_3O, our results have shown that there is not even a local minimum with an ion-pair configuration on the lowest potential surface. The local minimum on the excited 1 ^2E surface in C_{3v} geometry corresponding to H_3^+–O^- is not stable in lower symmetry. Analysis of the wave functions at points along the dissociation path in Fig. 6 shows that on distortion of the symmetric geometry, the system quickly loses its ion-pair character, becoming neutral H_3–O. The lowest state of H_3 is extremely repulsive with respect to $H_2 + H$. At the geometry of the H_3^+ equilibrium, for example, the H_3 ground state lies 81.9 kcal/mol above $H_2 + H$. Hence the H_3–O system readily dissociates to $H_2 + H + O$.

One may speculate that in any system where charge transfer leads to unstable neutral species, ion-pair states may not be stable. We have therefore undertaken calculations[35,36] on the Li_3H system as a counter example because both Li_3^+ and Li_3 are known to be stable. As will be reported elsewhere,[36] because the lowest state of Li_3H lies below all possible asymptotes, it is, indeed, predicted to be a stable species. However, it is not particularly energetic and the wave function involves substantial mixing between neutral and ion-pair configurations.

Relationship to other work

Our principal results for minima and transition states are displayed graphically in Fig. 7. We have also included the energy of the H_3O^+ ion placed by the experimental proton affinity corrected for zero-point energy.[21] The planar transition state for the reaction $OH + H_2 \rightarrow H_2O + H$ would appear at ~22 kcal/mol in Fig. 7 according to the reported 5.7–6.2 kcal/mol[13-15] barrier height, approximately 4 kcal/

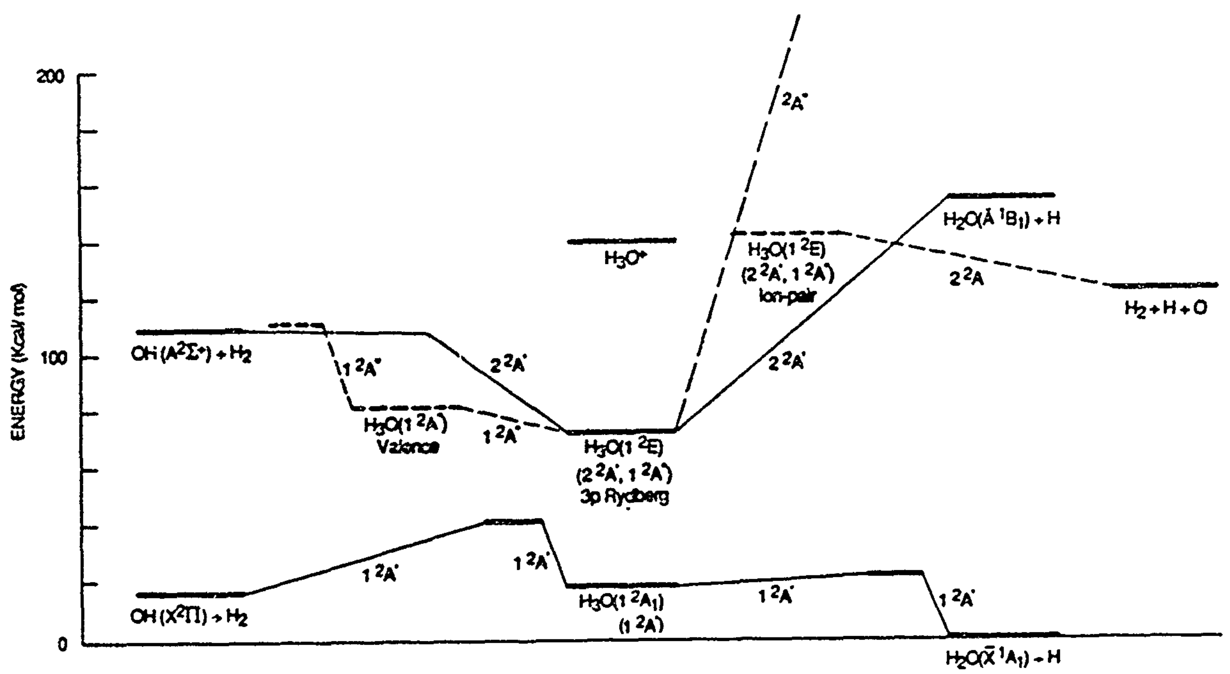

FIG. 7. Minima, transition states, and stationary points obtained in this work (MRSDCI energies) in relation to asymptotic energies. The dashed transition state on the $1\,^2A''$ potential surface connects to the OH + H + H asymptote (not shown). (See the text.)

mol above the $1\,^2A'$ state of H_3O. There does not, however, appear to be any connection between this planar geometry and the pyramidal geometry of the H_3O Rydberg states. In a brief search, we were unable to find any low energy path connecting the two geometries. Thus, we do not believe the planar transition state is relevant to the following discussion.

The present results may be discussed in view of the principal experimental findings for H_3O in the literature. Herzberg[11] has described an absence of discrete spectral features. Gellene and Porter[7] have reported observation of metastable D_3O with a lifetime $>0.6\ \mu s$ by charge-transfer and collisional reionization in K but find no evidence for H_3O. In a subsequent paper, Raskit and Porter[8] reported charge-transfer in Na leads to observation of $D_3{}^{16}O$ but not of $D_3{}^{18}O$ under identical conditions. The work of March and Young[10] leads to the conclusion that H_3O is not stable.

The discussion to date by Porter and co-workers[7,8] of the existence of H_3O has been based on the possible barrier to dissociation to $H_2O + H$ on the lowest potential surface of H_3O assuming that the lowest state is being formed.

The present work confirms the understanding presented previously,[6] i.e., that the vibrationless potential has a very small barrier, 3.58 kcal/mol from the present calculations for dissociation of the $1\,^2A'$ state of $H_2O + H$. The zero-point energy of the $1\,^2A'$ state is calculated to be 18.08 kcal/mol while that of the five real frequencies for the transition state is 14 90 kcal/mol. At the transition state, not only is there one less bound mode, but the remaining vibrations are slightly lower in energy. Including the vibrational energies, a barrier height of 0 4 kcal/mol is predicted. Scaling the vibrational energies at the minimum and the barrier by the square root of the reduced mass, which should be at least approximately valid, gives a barrier height including vibration for D_3O of 1.32 kcal/mol. Considering that the uncertainties in the calculation are larger than the barrier heights predicted for H_3O or D_3O and that dissociation by tunneling should be possible for both species, it is not possible to predict whether these calculated barriers on the $1\,^2A'$ surface account for the observation of D_3O, but not H_3O. Furthermore, any argument based on the spacing of vibrational levels in D_3O would also predict $D_3{}^{18}O$ to be stable, which was not observed.[8]

The dissociative nature of the lowest state would presumably explain the failure to observe any discrete spectra terminating on the lowest state. Herzberg, in fact, speculates that predissociation of possible upper states leads to the lack of discrete lines. We have examined the $3p$ state, one likely upper state, in the present work. The only candidate path is dissociation along the $1\,^2A''$ potential surface to the $OH(X) + H_2$ asymptote to which it correlates directly. Unfortunately, working in C_s symmetry, we have not been able to locate a transition state that leads directly to this asymptote. However, it may be argued that because the $OH(X) + H_2$ asymptote involves no Rydberg character, any path from the $3p$ Rydberg minimum to that asymptote would have to go through a change to valence character. Assuming the valence minimum located by MCSCF gradients is at least approximately correct, it provides an estimate of the minimum energy of a valence state of $^2A''$ symmetry and thus a lower limit to the dissociation barrier. When zero point energy is included, as shown in Table I, the $1\,^2A''$ Rydberg and valence minima are at virtually the same energy so that the $3p$ Rydberg state may dissociate without a barrier.

While our results for dissociation of the $3p$ state are not unambiguous, the lifetime of the state is most likely limited not by dissociation but by radiation. The predicted radiative

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lifetime of 18 ns might well preclude the $3p$ state being observed in any[7,9,10] of the charge transfer collisional reionziation experiments.

The energetics of neither the $3s$ nor $3p$ Rydberg states of H_3O is consistent with the observations of Gellene and Porter[7] who reported an ionization potential for D_3O of 4.3 eV. Using the experimental proton affinity, from our calculations, the lowest state is estimated to lie 5.27 eV below H_3O^+ and the $3p$ level 2.92 eV below H_3O^+. Raynor and Herschbach obtained values of 4.68 and 2.80 eV, respectively, from calculated virtual orbital energies using Koopman's theorem.

Not all of the experimental observations on H_3O and D_3O can be completely explained by our current knowledge of the potential surfaces of H_3O. Furthermore, the correlation of the $1\,^2A''$ state to the lowest $OH + H_2$ asymptote as well as the status of the MCSCF-determined minimum of valence character on the $1\,^2A''$ potential surface require further investigation. Despite considerable study both experimentally and theoretically, there remain substantial gaps in our understanding of the H_3O system.

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Appendix B

LOW-LYING STATES OF Li_3H: IS THERE AN ION-PAIR MINIMUM?

LOW-LYING STATES OF Li_3H: IS THERE AN ION-PAIR MINIMUM?

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The $1\,^1A'$, $1\,^1A''$, $1\,^3A'$, and $1\,^3A''$ states of Li_3H have been investigated at the MCSCF/SOCI level. The global minimum is a planar conformation of $^1A'$ symmetry. A local minimum on the same potential surface at a C_{3v} pyramidal geometry, of mixed ion-pair and covalent character, is found at a relative energy of 20.30 kcal/mol. The barrier height for isomerization is predicted to be 1.3 kcal/mol. The correlation diagram linking states of Li_3H to those of Li_3+H, $LiH+Li_2$ and Li_2H+Li is presented.

1. Introduction

There is considerable intrinsic interest in understanding novel bonding mechanisms in polyatomic molecules. In addition, stable states of molecules with high energy content are of potential practical significance for the development of new propellants [1]. Ion-pair states of small polyatomics have been suggested as potentially energetic species. Theoretical methods are ideally suited for predicting energies and stabilities of modest-sized molecules. However, the primary focus of much theoretical work has been on conventionally bonded molecules and ion-pair states remain largely unexplored.

We have undertaken, therefore, a survey of ion-pair and nearby states of polyatomic molecules composed of light atoms. For the case of H_3O, as reported in a previous paper [2], ion-pair attraction between H_3^+ and O^- does not lead to a stable state. The C_{3v} symmetry pyramidal geometry with O^- centered over H_3^+ in its equilateral triangle equilibrium geometry is a local minimum on the second potential energy surface of H_3O, but it is unstable with respect to dissociation to $O+H_2+H$. A predicted [3] pyramidal local minimum on the lowest potential surface of H_4 has also been shown [4,5] to be unstable with respect to geometric perturbations. Both of these observations have been qualitatively explained by noting that ground state neutral H_3 is not a stable species. Therefore, any back charge transfer from O^- or H^- to H_3^+ will lead to the neutral which is repulsive with respect to H_2+H.

In contrast, as suggested by Michels [6], the Li_3H molecule may be more likely to exist as a stable ion-pair because both Li_3^+ and Li_3 are bound species. Preliminary calculations by Michels and Montgommery [7] indicate a minimum on the lowest potential surface of Li_3H at a C_{3v} pyramidal geometry, as expected, from the equilateral equilibrium geometry of Li_3^+ for the ion-pair state. Hydrides of lithium, in general, have received substantial attention in recent years [8–13]. Composed of light atoms and thus readily calculable, they can serve as models of metal compounds and of clusters. Li_3H, in particular, has been included in surveys of lithium hydrides by Kato et al. [8] and by Cardelino et al. [9], who predicted a stable species with a planar geometry bound by 0.58 [8] (0.48 [9]) eV with respect to Li_2H+Li, calculated at the SCF level.

In this work, we have used an MCSCF/CI approach to investigate the lowest singlet and triplet states of Li_3H. Geometries have been optimized by MCSCF gradient techniques; for each symmetry the pyramidal geometries anticipated for ion-pair states have been included in the study. The correlation diagram linking these minima to different possible dissociation products has been established and the relative energetics provided within a consistent computational model.

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2. Calculations

Because we expect the ion-pair states of Li_3H to be described as Li_3^+–H^-, the basis set for H must be sufficiently diffuse to provide a good description of the anion. The 4s3p1d Gaussian basis set for H consists of a double-zeta plus polarization (DZP) basis [#1] augmented by two diffuse s (0.07, 0.02), two diffuse p (0.09, 0.03) and one d (1.0) function. With this basis set, the calculated electronic affinity of the hydrogen atom is 0.66 eV, in reasonable agreement with the experimental value of 0.75 eV [15].

For the Li atom, basis sets used in previous work [#2] were combined to give a DZP basis extended by one diffuse s exponent denoted 5s2p1d. For the ground state of the Li atom, the present basis yielded an SCF energy of −7.432413 hartree, compared to the Hartree–Fock limit [18], −7.432726 hartree. The adiabatic ionization potential of Li_3 calculated with this basis set at the second-order CI level (SOCI) is 4.06 eV, which may be compared with the experimental value of 4.35 ± 0.2 eV [19]. With the present (5s2p1d/4s3p1d) basis, the SCF energy for LiH at the equilibrium bond distance (3.016 a_0) is −7.986199 hartree as compared with the near Hartree–Fock value of Cade and Huo [20] of −7.987313 hartree. For Li_3H geometry optimization, a double-zeta Li basis was used [#3].

The active space for the MCSCF calculations of Li_3H included the four orbitals arising from the Li 2s and H 1s orbitals. Analogous active spaces were used for calculations on the fragment molecules. Geometries were optimized at the MCSCF level using analytic gradients and analytic second derivatives. For some symmetries, geometries were obtained by direct variation of parameters. Energies at the minima were obtained from second-order CI (SOCI) calculations that included all single and double excitations from the active space. Calculations were carried out in C_s symmetry. In $^1A'$, $^1A''$, $^3A'$, and $^3A''$ symmetry, the SOCI expansion resulted in 16884, 16274, 22275, and 22596 configurations, respectively. The GAMESS [21] and ALCHEMY II [22] programs have been used in this work.

[#1] The two inner s functions were taken from the basis listed in ref. [14]. The p exponent was 0.9.

[#2] The five s functions were taken from the first five functions listed by Gerber and Schumacher [16]. The third s was replaced by an exponent of 0.45. The p and d functions were taken from the F, G basis set of McAdon and Goddard [17].

[#3] For the Li double-zeta basis the two most diffuse s functions were replaced by a single function with an exponent of 0.055 and the d function was omitted.

3. Results and discussion

3.1. Fragment geometries and energies

In order to obtain dissociation energies with respect to all possible asymptotes within a consistent computational model and to compare present work with previous calculations and with experiment, comparable MCSCF/SOCI calculations have been performed for the diatomics Li_2 and LiH and for the triatomics Li_3, Li_2H, and Li_3^+.

Numerous calculations of Li_2 and LiH have appeared in the literature; only representative examples [13,23] are included in table 1. The discrepancy of the calculated dissociation energies with the experimental values is 1.2 and 3.9 kcal/mol for Li_2 and LiH, respectively. Core polarization has not been included in the present calculations [26].

The lowest two states of Li_3, which are predicted [9,16,17,27,28] to have C_{2v} symmetry, are nearly degenerate in energy. Therefore, there has been considerable work devoted to determining the ground state. As shown in table 2, in agreement with previous work, we predict a $^2B_2$ ground state with the $^2A_1$ state lying 0.56 kcal/mol higher in energy. Geometries for both states are in reasonable agreement with previous calculations. The predicted atomization energy of the ground state lies 3 kcal/mol outside the error bars of the experimental determination [19]. The optimized C_{3v} symmetry geometry for Li_3^+ is also listed in table 2.

The ground state of the Li_2H molecule is a $^2A_1$ state in C_{2v} symmetry, while the first excited state is predicted to be a symmetric linear species of $^2\Sigma_u^+$ symmetry, lying 9.67 kcal/mol higher in energy. Results of previous calculations are also summarized in table 3.

Table 1
Comparison of calculated results for Li_2 and LiH with experiment and previous calculations

	Li_2			LiH		
	present work	calc. [23]	exp. [24]	present work	calc. [13]	exp. [25]
basis set	5s2p1d	12s7p2d		5s2p1d/4s3p1d	4s4p2d1f/4s2p1d	
calculation	MCSCF/SOCI	CPP+CI [a]		MCSCF/SOCI	CEPA [b]	
R_e (Å)	2.673 [c]	2.676	2.673	1.596 [c]	1.599	1.596
D_e (kcal/mol)	23.14	24.20	24.36	54.11	57.15	57.98

[a] Core polarization potential+CI (valence). [b] Correlated electron pair approximation. [c] Experimental value.

Table 2
Comparison of calculated results for Li_3^+, Li_3($^2B_2$), and Li_3($^2A_1$) states with experiment and previous calculations

	Calculations						Experiment [19]
	present work	ref. [27]	ref. [16]	ref. [28]	ref. [17]	ref. [9]	
basis set	5s2p1d	4s3p	6s3p1d	4s2p	3s2p	9s5p (uncontracted)	
calculation	MCSCF/ SOCI	valence CI+S+D	CEPA	SCF +S+D	GVB/ CI	SCF	
Li_3^+($^1A_1$) Li / \ r Li — Li	C_{3v} symmetry						
r (Å)	3.099			3.084		3.040	
Li_3($^2B_2$) Li / \ r_1 Li — Li r_2	C_{2v} symmetry						
r_1 (Å)	2.820 [a]	2.80	2.768	2.45	2.869	2.851	
r_2 (Å)	3.271 [a]	3.18	3.235	2.9	3.352	3.188	
D_e (kcal/mol) [b]	35.68	29.41	34.40	28.76			41.5 ±4
D_0 (kcal/mol)	34.5 [c]		33.25				4.35±2
IP (eV) (adiabatic)	4.06		4.0	3.95			
Li_3($^2A_1$)	C_{2v} symmetry						
r_1 (Å)	3.041	3.07	3.011		3.138	3.245	
r_2 (Å)	2.756	2.70	2.730		2.761	2.692	
T_e (kcal/mol)	0.56	0	0.69		0.19	2.17	

[a] Gradient optimization. [b] Dissociation to 3Li. [c] Estimated from vibronic levels calculated in ref. [16].

3.2. Li_3H geometries

Optimized geometrical parameters for the 1 $^1A'$, 1 $^3A''$, and 1 $^3A'$ symmetries of Li_3H are listed in table 4 and energies are given in table 5. The symmetry plane of C_s symmetry contains H and Li′ and bisects the Li–Li bond, as denoted in fig. 1. The global minimum is a planar geometry of A′ symmetry, in agree-

Table 3
Comparison of calculated results for $Li_2H(^2A_1)$ and $Li_2H(^2\Sigma_u^+)$ states with previous calculations

	Present work	Ref. [8]	Ref. [9]	Ref. [10]
basis set	5s2p1d/4s3p1d	5-21G/2s	9s5p/9s5p	4s3p/3s1p
calculation	MCSCF/ SOCI	SCF	SCF	SCF/ valence CI
$^2A_1$ H / \ Li Li	C_{2v} symmetry			
Li-H (Å)	1.730 [a]	1.764	1.719	1.720
Li-Li (Å)	2.564 [a]	2.611	2.514	2.536
D_e (kcal/mol) [b]	24.22	18.90	21.66	22.4
$^2\Sigma_u^+$ Li-H-Li				
Li-H (Å)	1.705		1.684	1.70
T_e (kcal/mol)	9.67		10.28	8.50

[a] Gradient optimization Li basis 5s2p. [b] With respect to LiH + Li.

Table 4
Optimized geometrical parameters [a] for Li_3H

			Ref. [8] [b]	Ref. [9] [c]
1 ¹A′ planar (C_s)	Li-Li	1.769	1.781	1.740
	Li′-H	3.963	4.185	4.092
	Li-Li′	3.066	3.239	3.118
	Li-Li	2.617	2.599	2.466
			Ref. [7] [d]	
1 ¹A′ pyramid (C_{3v})	Li-Li	2.737	2.599 (2.664)	
	Li-H	1.840	1.886 (1.896)	
	d	0.942	1.142 (1.109)	
1 ¹A′ transition state pyramid→planar	Li-H	1.824		
	Li′-H	1.860		
	Li-Li′	2.708		
	Li-Li	2.815		
			Ref. [8] [b]	
1 ³A″ planar (C_s)	Li-H	1.754	1.772	
	Li′-H	3.561	3.609	
	Li-Li′	3.014	3.085	
	Li-Li	2.966	3.028	
1 ³A′ [e] pyramid (C_s)	Li-H	1.716		
	Li′-H	1.858		
	Li-Li′	3.206		
	Li-Li	2.549		

[a] Defined in fig. 1, distances in Å. [b] Calculation of Kato et al. [8] described in the third column of table 3.
[c] Calculation of Cardelino et al. [9] described in the fourth column of table 3. [d] 6-311G**/SCF (3-21G**/MP2).
[e] One imaginary frequency, 277i cm^{-1}.

Table 5
Calculated energies for Li_3H system

	Total energy (hartree)		Relative energy [a)] (kcal/mol)	Zero-point energy [b)] (kcal/mol)
	MCSCF	SOCI		
$Li_3H(^1A')$ planar	−22.938538	−22.974132	0.0	4.66
$Li_3H(1\,^1A')$ C_{3v} pyramidal	−22.901177	−22.941791	20.30	3.75
$Li_3H(1\,^1A')$ transition state pyramid→planar	−22.901130	−22.939750	21.58	3.72
$Li_3H(1\,^3A'')$ planar	−22.919232	−22.945625	17.89	4.42
$Li_3H(1\,^3A')$ C_s pyramidal	−22.905243	−22.939508	21.73	
$LiH+Li_2(X\,^1\Sigma_g^+)$ [c)]	−22.881967	−22.918979	34.62	2.01 [d)]
$Li_2H(^2A_1)+Li$ [c)]	−22.892861	−22.921818	32.83	
$Li_2H(^2\Sigma_u^+)+Li$ [c)]	−22.882581	−22.906410	42.50	
$Li_3(^2B_2)+H$	−22.827279	−22.853793	75.54	
$Li_3(^2A_1)+H$ [c)]	−22.826337	−22.852909	76.09	

[a)] With respect to $Li_3H(^1A')$ planar geometry. SOCI calculation. [b)] MCSCF calculation 4s2p/4s3p1d basis.
[c)] Supermolecule calculations. [d)] Li_2 spectroscopic value [26].

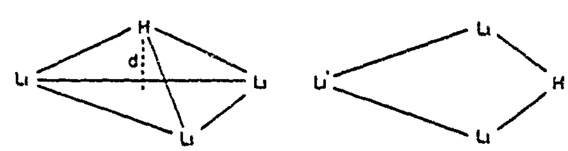

Fig. 1. Geometry of pyramidal and planar conformations of Li_3H. The vertical distance from the apex of the pyramid to the plane of the three Li atoms is denoted by *d*.

ment with previous work [8,9]. A C_{3v} pyramidal structure, anticipated for the ion-pair state, is found to be a local minimum with all real vibrational frequencies, 20.3 kcal/mol above the planar minimum. A comparison with geometries reported by Michels and Montgomery [7] for this state is also included. Differences up to 0.2 Å in bond length due to differences in basis set and computational model may be noted. The transition state for conversion of the pyramidal form to the planar geometry has also been determined. It is predicted to have a low imaginary frequency, 120i cm^{-1}, and to occur at a very modest geometrical distortion from the pyramid, with a calculated barrier height including zero-point energy of 1.3 kcal/mol.

The lowest triplet state, $1\,^3A''$, has a planar minimum geometry that lies 17.9 kcal/mol above the planar singlet ground state. We were not able to determine a pyramidal local minimum for the $^3A''$ state. Restricted to C_s symmetry, the $1\,^3A$ state has a stationary point at a pyramidal geometry with one imaginary frequency, 277i cm^{-1}. An approximate investigation of the $1\,^1A''$ state gave a pyramidal (C_s symmetry) form 14 kcal/mol above the $1\,^3A'$ state. The $1\,^3A'$ and $1\,^1A''$ states in planar geometries were found not to be stable with respect to the $Li_2H(^2A_1)+Li$ and $Li_2H(^2\Sigma_u^+)+Li$ asymptotes, respectively, with which they correlate

3.3. Correlation diagram

The correlation diagram linking the states of Li_3H to those of Li_3+H, $LiH+Li_2$, and Li_2H+Li is shown in fig. 2. The correlations have been drawn preserving the C_s symmetry plane described above, containing the H and Li′ atoms. Energies of the Li_3+H and Li_2H+Li asymptotes and for the lowest $LiH+Li_2$

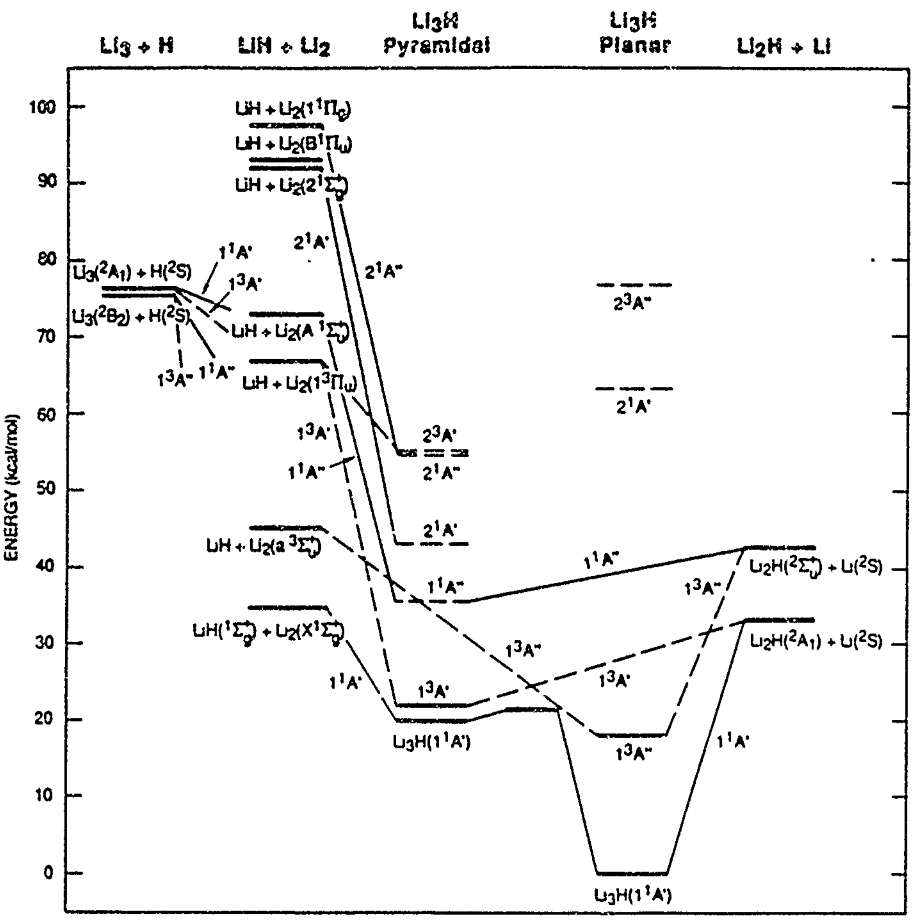

Fig. 2. Correlation diagram linking the states of Li_3H to those of Li_3 + H, LiH + Li_2, and Li_2H + Li has been drawn preserving C_s symmetry (see text). The second state of each symmetry, shown by a dashed line, has been calculated at the geometry of the lower state.

asymptote, listed in table 5, have been calculated for the supermolecule. Optimized geometries for the triatomics, tables 2 and 3, have been used. Excitation energies for the states of Li_2 were taken from tabulated T_e values [25] and from the calculations of Schmidt-Mink et al. [23] for the non-observed $a\,^3\Sigma_u^+$, $1\,^3\Pi_u$, $2\,^1\Sigma_g^+$, and $1\,^1\Pi_g$ states.

The lowest state of each symmetry is clearly bound with respect to all possible separated fragment asymptotes. The diagram also includes the second state of each symmetry at the geometry of the ground state. The energies are of qualitative reliability only because, except for the $2\,^2A'$ state, these states involve excitation to molecular orbitals not included in the MCSCF active space. They are, however, predicted to be bound with respect to the LiH + Li_2 asymptotes to which they correlate.

4. Discussion

One goal of this work was to investigate whether ion-pair attraction in Li_3H, unlike the cases containing H_3^+ as the positive ion, leads to a stable energetic state. There is only one state, a $^1A'$, arising from the $Li_3^+(^1A_1) + H^-$ limit, which would lie at 152 kcal/mol in fig. 2 (not shown). Analysis of the wavefunction of the $1\,^1A'$ state at the C_{3v} pyramidal structure indicates substantial mixing of ion-pair and covalent bonding character. The Li–Li bond length of 2.737 Å is 0.36 Å shorter than the corresponding bond length in Li_3^+, in contrast to the case [2] of H_3O, where the ion-pair state was found at the H–H separation of H_3^+. Both Li–Li bond lengths in the C_{2v} structure of $Li_3(^2A_1)$, to which this state correlates, are longer as well.

The prediction of a true minimum on the $1\,^1A'$ surface (all real frequencies) at the C_{3v} geometry of mixed ionic and covalent character supports the original suggestion [6] that because of the stability of Li_3 and Li_3^+, back charge transfer will not limit the stability of Li_3H with respect to dissociation. Unlike the H_4 and H_3O examples considered previously [2–5], there is in this molecule, a lower energy planar form. Given the very low (1.3 kcal/mol) calculated barrier to interconversion, the pyramidal local minimum is predicted to be unstable relative to the global planar minimum. While the lowest state of Li_3H is most definitely stable, it is not particularly energetic.

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