

The OBeH₂ hypersurface: Local and global minima, transition states, and reaction paths

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The lowest singlet potential energy surfaces of OBeH₂ and its isomers are calculated, using geometry optimization techniques at the Fermi–Sea-multiconfiguration-self-consistent-field level. The reaction paths going from one isomer to the others are mapped and the appropriate transition states are located and verified. It is shown that, although the transition from BeO + H₂ to OBeH₂ is virtually barrierless, it can be achieved by an approach of molecular hydrogen to BeO from the Be side at right angles only. It is also shown that, should OBeH₂ be formed, the transition to other, energetically lower points on the potential energy surface, involves twisting of the H₂ moiety, thus making subsequent formation of linear H–O–Be–H the only option. The energy release upon this isomerization is 71 kcal/mol, while the activation barrier is 10 kcal/mol.

I. INTRODUCTION

Recently, it was shown^{1,2} that OBeH₂ exists in a local minimum of its potential energy surface (PES), where H₂ remains in molecular form, albeit with a slightly weakened bond. This exceptional situation is caused by the parallel action of the doubly occupied σ bond of H₂, which is polarized by the “Be²⁺” ion, and of the σ^* single excitation in H₂ which interacts weakly with the low-lying virtual orbitals of the metal atom positive ion. Similar studies on other compounds containing a nontransition metal or metal–metal bond, produced results which can be interpreted in the same way.^{1–3} In fact, it was the search for such minima on multidimensional surfaces that started our investigations in this direction.¹

The particular characteristics of the prototype OBeH₂ as regards its existence in a local minimum and its ability to trap H₂ in molecular form, offer an intriguing opportunity for studying computationally the full PES of the lowest singlet state, mapping in detail the minima and the transition states of this four atom system, and trying to gain insights into the mechanisms of reaction and stability. This paper reports the results of such an extensive study.

It should be noted that for systems of two or three atoms where symmetry is often present, PES are frequently mapped out in detail, as it is usually possible to reduce these surfaces to three-dimensional ones, or even two-dimensional curves.⁴ However, for systems possessing four or more atoms, PES are rarely calculated in full or mapped out in any detail, since the multidimensionality of the problem usually defeats conventional approaches, except in rare cases where exceptionally high symmetry is present. Often the project is reduced to locating stationary points on the surface.⁵ However, this approach implies some previous knowledge of what one expects to find. In cases where such information is not available, two techniques are possible. Either, by judicious use of chemical intuition, one keeps some internal coordinates constant throughout, thus reducing the problem to three dimensions or less,⁶ or one

follows the more laborious route of multiple geometry optimizations.⁷ This technique, which shall be described in detail in the following section, is the one we have chosen for the present problem.

II. COMPUTATIONAL DETAILS, METHOD, AND APPROXIMATIONS

OBeH₂ contains four atoms, and its geometry is therefore defined by 12 Cartesian coordinates. If one defines instead internal coordinates, only six are needed, i.e., the PES has six degrees of freedom and, in principle, we should compute a seven-dimensional PES (the seventh dimension being the energy) in order to map the reaction paths connecting the various local and/or global minima and to locate the transition states through which these paths must pass.

The magnitude of a computational project involving a seven-dimension PES is extraordinary. Indeed, presently it is impractical to compute that many points. Moreover, even if such a task were undertaken, the resulting surface would be of little use, being impossible either to depict graphically or to interpret in any chemically meaningful way. It is therefore imperative to adopt a strategy, whereby the seven-dimensional PES can be reduced to a tractable three-dimensional one.

Such an idea has already been applied successfully.⁸ It involves choosing two coordinates out of the many involved in the hypersurface, such that these will form the reaction coordinates in a three-dimensional space. For each pair of values of these two coordinates, all others are optimized. The three-dimensional surface thus generated is a minimum with respect to all degrees of freedom except those chosen as the reaction path.

In the present case, the following six internal coordinates were chosen:

- (i) The distance $R_{\text{O-Be}}$ between the oxygen and beryllium atoms.
- (ii) The distance $R_{\text{Be-H}_2}$ between the beryllium atom

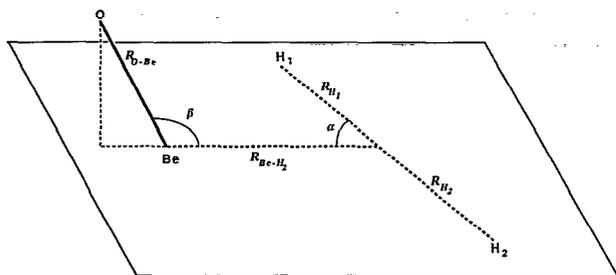


FIG. 1. Internal coordinates used in the OBeH₂ PES calculation. See the text for details.

and the intersection of the line connecting the two H atoms with the projection of the O-Be line on the BeH₂ plane. This distance was taken to be positive when the intersection lay on the side of Be opposite from O, and negative otherwise.

(iii) The angle α between the H-H line and the O-Be line.

(iv) The distance R_{H_1} from the H-H and O-Be line intersection to the first hydrogen atom.

(v) The distance R_{H_2} from the above intersection to the second hydrogen atom.

(vi) The out-of-plane bend angle β of the O-Be bond with the Be-H₂ plane.

The above coordinates are exhibited in Fig. 1.

All geometry optimizations were carried out by employing correlated wave functions computed at the Fermi-Sea (FS)-multiconfiguration-self-consistent-field (MCSCF) level, using the MULTI part of the MOLPRO package.⁹ The Fermi-Sea is the set of zeroth order occupied and vacant spin orbitals which are deemed to be the most important for the state of the PES of interest. The choice of the FS orbitals follows guidelines determined by a combination of empirical with *a priori* rules.^{10,11}

The molecule has 14 electrons and the FS zeroth-order space consisted of 12 orbitals. Of these, three, i.e., the oxygen and beryllium 1s orbitals and one oxygen lone pair, were kept doubly occupied at all times. Since no symmetry constraints were imposed at any time (C_1 symmetry), this gives a total of 5992 MCSCF configurations. This is the same space used in our previous calculation of the OBeH₂ geometry.¹ To thoroughly test the assumptions of this approximation, several calculations were performed at key points on the surface keeping only the oxygen and beryllium 1s orbitals always doubly occupied. This raised the number of configurations to 60 000, with a tremendous increase in the time required for each MCSCF calculation, without significantly affecting the energetics.

The initial surface was generated keeping R_{O-Be} and R_{Be-H_2} fixed. R_{O-Be} ranged in value from 2.0 to 9.5 atomic units (a.u.) in increments of 0.5 a.u., while R_{Be-H_2} ranged in value from 9.5 to -9.5 a.u. in increments of 1.0 a.u. Thus a total of 320 points were calculated as a start. Moreover, additional calculations at or around significant parts of the surface were performed, in order to increase the accuracy of the resulting picture. Since each point involved

optimization of four internal coordinates, i.e., an average of ten MCSCF calculations, the surface generated involved around 4500 MCSCF energy and an equal number of MCSCF gradient calculations.

A number of points on the surface gave the appearance of transition states. This possibility was tested by force constant calculations at the appropriate geometries and/or transition state searches in the neighborhood of those geometries. All such calculations were carried out using the GAMESS¹⁵ code at the FS-MCSCF level, using the same spaces and approximations as before.

It was subsequently deemed necessary to generate a second surface, orthogonal to the first, this time keeping R_{Be-H_2} and α fixed. The range was the same as before, while the α values ranged from 60° to 120°, in increments of 5° (it should be noted here that one only needs to calculate the PES for values of α ranging from 30° to 90°, as the rest are identical by symmetry). A considerable number of additional calculations were performed at or near critical points or interesting features of the surface. Thus a further 200 or so points were generated, bringing the total number of MCSCF energy (and corresponding gradient) calculations to well over 6500.

Building on the information gathered by the study of the two surfaces, a potential energy curve was later calculated, showing the reaction path from one part of the PES to another.

All calculations were performed using standard Dunning-Hay¹⁶ double zeta bases, augmented by single polarization functions for all atoms (p with exponent 1.0 for H and d with exponents 0.6 and 0.85, respectively, for Be and O).¹⁶ This basis set has been shown to give, in past calculations, both a good qualitative picture and reliable enough energetics. In view of the great number of calculations involved in the present work, a larger basis set would have increased the task by an unacceptable factor, while a smaller, split valence-type basis set, could, in certain cases, have given unreliable results.

III. ISOMERS OF OBeH₂

The calculations which are described in the previous section have shown the existence of the following minima (in order of increasing energy), on the Be + O + H₂ hypersurface:

$$\text{H-O-Be-H} \quad -90.8354 \text{ a.u.},$$

$$\text{H}_2\text{O} + \text{Be} \quad -90.7352 \text{ a.u.},$$

$$\text{OBeH}_2 \quad -90.7229 \text{ a.u.},$$

$$\text{BeO} + \text{H}_2 \quad -90.6953 \text{ a.u.},$$

$$\text{O} + \text{BeH}_2 \quad -90.5354 \text{ a.u.}$$

The geometries of the above isomers are shown in Fig. 2, while their geometrical parameters, together with those of the transition state described in the next section, are shown in Table I. If one were to take OBeH₂ as a point of reference, it is quite easy to see the topological relationship between this species and those lying above it in energy. To

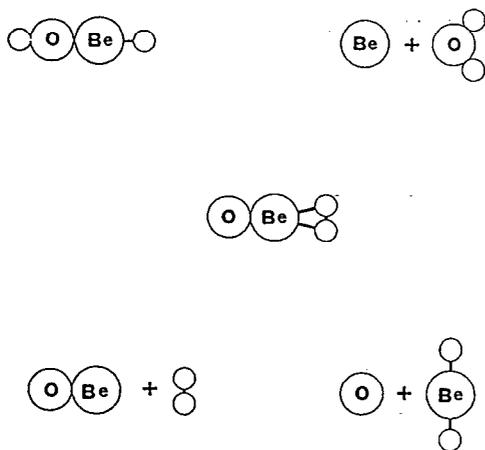


FIG. 2. Isomers of OBeH₂. Top left: H-Be-O-H; Top right: Be+H₂O; Center: OBeH₂; Bottom left: BeO+H₂; Bottom right: O+BeH₂.

go from OBeH₂ to (BeO+H₂), one merely has to “pull” the H₂ moiety away from the molecule. Similarly, to go from OBeH₂ to (O+BeH₂), one has to pull the O atom away, from the other side.

Things are not as simple when trying to go from OBeH₂ to the two species lying below it in energy. To produce the (H₂O+Be) geometry, one has to imagine the H₂ moiety moving from one side of Be to the other, then away from Be and towards O, until it is “released” by Be and “captured” by O.

In an even more complicated way, one can move from the OBeH₂ geometry to that of H-O-Be-H. The latter is a linear molecule, therefore the transition involves a twisting of the H₂ moiety with simulations lengthening of the Be-H bond length lying closest to O, until the H atom moves away from Be and on the other side of O.

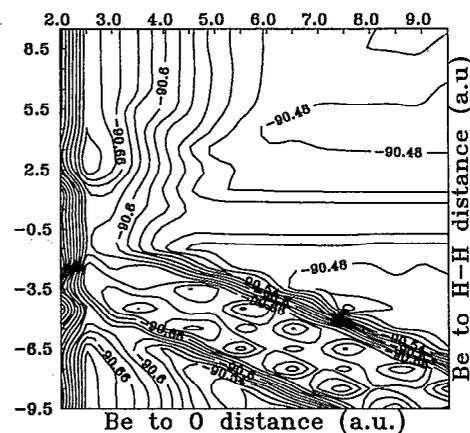
Mapping the paths that interconnect the various isomers shown above, in a way which is computationally feasible, qualitatively correct, and quantitatively acceptable, and which at the same time allows for easy chemical interpretation, has been the goal of the present work.

IV. RESULTS AND DISCUSSION

The first surface described in Sec. II is depicted in Fig. 3(a) as a contour map and in Fig. 3(b) as a three-

TABLE I. Internal coordinates (where defined) and energies of all stable and metastable species on the OBeH₂ hypersurface, plus the transition state going from OBeH₂ to HBeOH. All distances are in a.u. and all angles are in degrees.

Species	R_{O-Be}	R_{Be-H_2}	α	R_{H_1}	R_{H_2}	β	R_{H-H}	Energy
HBeOH	2.635	0.0	180.0	2.534	4.432	0.0	6.966	-90.8354
Be+H ₂ O							2.874	-90.7352
OBeH ₂	2.563	2.895	90.0	0.730	0.730	0.0		-90.7229
BeO+H ₂	2.572						1.440	-90.6953
O+BeH ₂		0.0	90.0	2.521	2.564		5.085	-90.5354
Trans. state	2.594	2.672	180.0	0.391	1.151	0.0	1.542	-90.7053



start with BeO and approach with the H_2 molecule at a right angle to the BeO line and from the Be side [i.e., start at position (2.6, 9.5) on the map]. Indeed, this is the *only* way to get there, if one discounts starting with $\text{O} + \text{BeH}_2$ [position (9.5, 0.0) on the map]. Actually, this latter possibility must be discounted, since one must start at a point energetically much higher (more than 100 Kcal/mol) than $\text{BeO} + \text{H}_2$ and involving atomic oxygen, a very reactive species. This approach to BeO by H_2 can be seen to be barrierless. Nevertheless, it is a path of low probability, as any approach of H_2 other than from the Be side will not lead to formation of OBeH_2 . We shall discuss this in greater detail later.

Starting at approximately the position (2.6, -3.0) and continuing to the lower right-hand corner of the contour map [position (9.5, -9.5)] we see a valley of energies lower than OBeH_2 . These represent $\text{Be} + \text{H}_2\text{O}$. In fact, there are *two* valleys, separated by a ridge, representing the two forms of $\text{Be} + \text{H}_2\text{O}$, where H_2 is either between Be and O , or on the side of O opposite that of Be . $\text{Be} + \text{H}_2\text{O}$ represents another local minimum on the PES, lower than OBeH_2 by about 10 Kcal/mol. The apparent holelike irregularities in the valleys are more artifacts of the contouring program than real features of the surface. It should be noted that the interaction of Be with H_2O has been the subject of several previous investigations,¹⁷ some of which found that a complex (planar or bent) was formed, having an energy of about 1 kcal/mol lower than free $\text{Be} + \text{H}_2\text{O}$. We did not notice such a complex but its existence was not part of the present investigation and was not pursued in any detail.

Finally, at approximately (2.6, -9.5), we find $\text{BeO} + \text{H}_2$ again, with H_2 approaching BeO from the O side this time.

If one inspects the contour map, there appears to be a barrier separating OBeH_2 and $\text{Be} + \text{H}_2\text{O}$, in the form of what appears to be saddle point. In fact, the process of going from one to the other seems to be that described above, in Sec. III. To test the existence of this transition state, a saddle point location search was initiated using the GAMESS¹⁵ code. A stationary point was indeed located, more than 60 kcal/mol above OBeH_2 , but on performing a vibrational analysis, it was found that it had *two* imaginary frequencies, and was therefore not a saddle point, but a stationary point around which there exists an alternative path. This was not found to be true of the transition state separating $\text{BeO} + \text{H}_2$ (with H_2 on the O side) and $\text{H}_2\text{O} + \text{Be}$, which proved to have only one imaginary frequency and to be a true saddle point. The barrier separating $\text{BeO} + \text{H}_2$ from $\text{H}_2\text{O} + \text{Be}$, however, was found to be more than 45 kcal/mol, making it highly unlikely that $\text{BeO} + \text{H}_2$ will react to form $\text{H}_2\text{O} + \text{Be}$, even if the true barriers were somewhat lower.

So the question is whether, apart from bringing Be and H_2O together, there is another way to reach this isomer, such as starting from OBeH_2 . Since the apparent transition state on the first PES, apart from being too high, was also proved to be false, it remains to see where the path around leads. To do this we calculated another three-dimensional

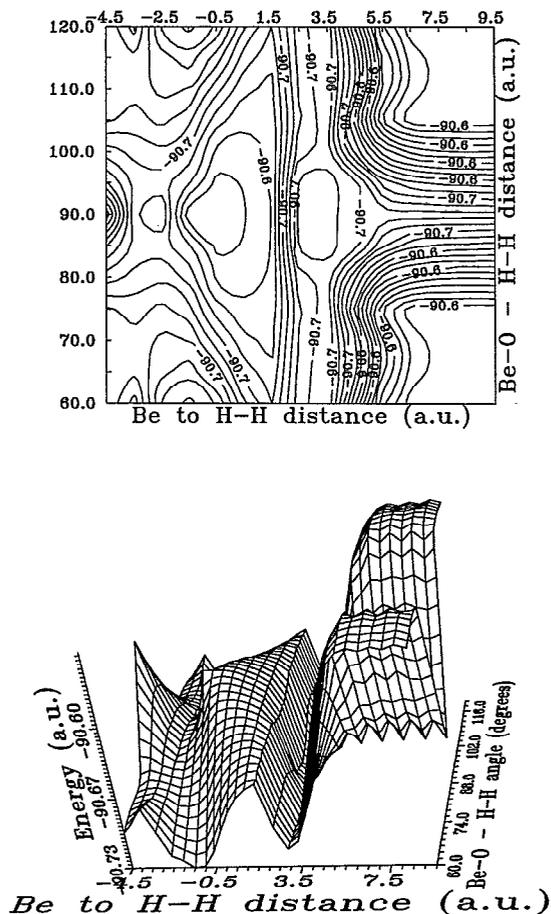


FIG. 4. (a) Contour map of part of the OBeH_2 surface. The X axis is the $R_{\text{Be-H}_2}$ distance, in a.u., while the Y axis is the angle α , in degrees. Note the narrow valley leading to the OBeH_2 local minimum, with very high areas on both sides of it, and the elongated minimum around this local minimum, in the α direction. (b) The same surface as in (a), shown as a three-dimensional mesh.

surface, by keeping $R_{\text{Be-H}_2}$ and α fixed this time, and for one particular value of $R_{\text{O-Be}}$ already calculated, 2.5 a.u. This means that we now had to optimize *three* internal coordinates, R_{H_1} , R_{H_2} , and β , for each point, instead of four.

This new surface is shown in Fig. 4(a) as a contour map and in Fig. 4(b) as a three-dimensional mesh. The first thing we notice is that, apart from a very narrow valley leading to OBeH_2 , which represents a "right angles" approach of H_2 to BeO , all other approaches are extremely high in energy, meaning that H_2 and BeO will not interact unless the right angles condition is met. In other words, if H_2 approaches BeO at any other angle, it will "hit" a very high energy "wall." This wall is uniformly steep, and has only one way through. Unlike most surfaces, there is little here to guide or "turn" H_2 so that it can interact with BeO , since the opening leading to OBeH_2 appears suddenly, with no gradual change of slope, and is very small. Definitive answers as to the probability of such a reaction can, of course, be given only with dynamics calculations.

The second thing we notice, is an elongated minimum

area surrounding the OBeH₂ local minimum. Inspection of the actual changes in all internal coordinates, shows that what actually happens is that the H₂ moiety “slides” around the Be atom, moving towards the top, i.e., tending to become parallel to the Be–O line. Its distance from the Be atom remains essentially unchanged throughout, while the energy goes up by no more than 10 kcal/mol. How can such a drastic geometry change be accompanied by such a small energy change? The answer lies in the “looseness” of the Be–H₂ “nonclassical” bond, which has been discussed in detail elsewhere.¹

What lies outside this elongated minimum area? The scheme employed in this surface breaks down as the angle α moves more than 30° away from 90°, because for values of $R_{\text{Be-H}_2}$ different than the optimum for the Be–H₂ bond, the geometry contortions imposed are too drastic for the gradient algorithm to locate a partial minimum. Moreover, the concept of “positive” and “negative” $R_{\text{Be-H}_2}$ values loses meaning when H₂ becomes parallel (or almost parallel) to Be–O. However, it is obvious that, once more, one of the internal coordinates, i.e., $R_{\text{Be-H}_2}$, remains unchanged for all practical purposes, due again to the nature of the Be–H₂ nonclassical bond, which remains unbroken despite the movement of H₂ around and over Be. This gives us the opportunity to reduce the three-dimensional surface under consideration to a two-dimensional curve, keeping only α fixed and optimizing *everything else*. Once a value of 0° is reached for α , the transition state has essentially been located, and from there on, the reaction coordinate changes from α to the distance from the Be–O line to the H–H line.

This curve is shown in Fig. 5. It shows a local minimum for OBeH₂, a transition state at $\alpha = 180^\circ$, and a minimum on the other side. This minimum is the *absolute* minimum of the global PES, and is the linear entity H–Be–O–H. It should be noted that the X axis of the curve is in fact the *reaction coordinate* going from Be–O + H₂. It is the angle α only between 90° and 180°. In between these values the H–H distance remains practically constant and equal to 1.4 a.u., i.e., the H₂ moiety remains intact. Also between these values of α , the $R_{\text{Be-H}_2}$ distance remains practically constant. For $\alpha < 90^\circ$, the reaction coordinate becomes $R_{\text{Be-H}_2}$, while for $\alpha > 180^\circ$ it becomes the distance between the Be–O and H–H lines, with α retaining a value of 90° in the former case and 180° (or 0°) in the latter case.

The geometries along the curve are shown by pictures above it while the actual transition state geometry is shown in Fig. 6. This transition state was tested through a vibrational analysis, and was found to possess only one imaginary frequency, i.e., to be a true saddle point. Moreover, it was found to lie only 10 kcal/mol above OBeH₂, as opposed to 16 kcal/mol needed to release H₂ trapped by BeO.

There remains therefore only one other way in which Be + H₂O can be reached from OBeH₂, i.e., through a change of β . This means that the H₂ moiety, instead of moving on either side of Be towards O, could conceivably move *out of the plane, around* Be. This possibility was tested through detailed calculations. However, it was found that the energy needed to do this, was more than that needed to remove H₂ and give BeO + H₂. Therefore,

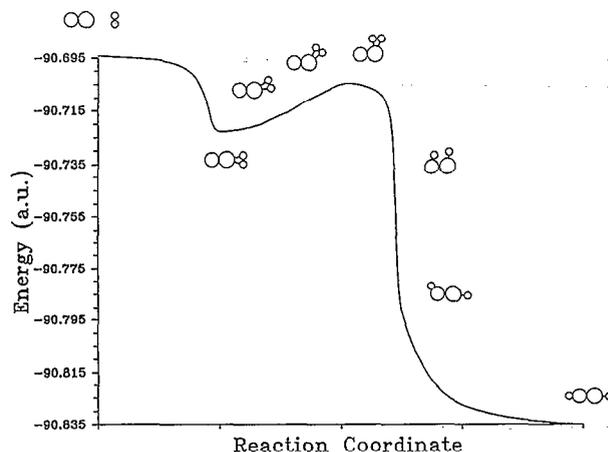


FIG. 5. Potential energy curve of the transition from BeO + H₂ to OBeH₂ and subsequently to H–Be–O–H. The X axis is the reaction path, i.e., it is the $R_{\text{Be-H}_2}$ distance up to the first tick mark, the α angle between the first and second tick marks, and the distance between the Be–O and H–H lines thereafter. All other internal coordinates are optimized at all times. The geometries of the species along the reaction path are shown above or below the curve.

we must conclude that reaching the Be + H₂O valley in any other way than bringing Be and H₂O together is not feasible.

V. CONCLUSION

Reliable computation of the OBeH₂ potential energy hypersurface has led to the following conclusions:

(a) The formation of OBeH₂, which exists in a local minimum, can take place only if H₂ approaches BeO from the Be side at right angles.

(b) Formation of OBeH₂ is guided by the shape of the surface, or more simply, the energy curve in Fig. 5. Since the transition from BeO + H₂ to OBeH₂ is barrierless and involves an energy release of 16 kcal/mol, and since the barrier separating OBeH₂ from H–O–Be–H is only 10 kcal/mol, transformation of reaction energy to vibrational energy is required. Fitting of the curve in Fig. 5 shows that as many as 19 vibrational levels are supported, i.e., the

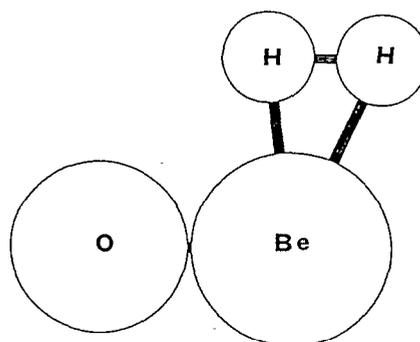


FIG. 6. Geometry of the transition state separating OBeH₂ and H–Be–O–H.

probability of OBeH₂ staying in the local minimum is certainly non-negligible. Here, again, the definitive answer can be supplied by dynamics calculations.

Once in the local minimum, OBeH₂ could move away only by tunneling or by the supply of enough activation energy. Moreover, in the latter case, it would *always* change to H–O–Be–H, thus giving off a large amount of energy, as less energy is needed to effect this transition than to release the H₂ trapped by BeO.

(c) Be + H₂O can only exist if Be and H₂O are brought together and not by any other path on the PES under investigation.

Finally, on the practical side of matters of catalysis and of energy transfer, the above facts suggest that as an energy and hydrogen storage possibility, OBeH₂ and similar molecules with volcanic ground surfaces^{1–3} offer possibilities for further investigations, in the gas or in the solid phase.

ACKNOWLEDGMENTS

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