

Proton and Li⁺ Cation Interactions with H₂O₃ and H₂O/O₂: *Ab Initio* Molecular Orbital Study

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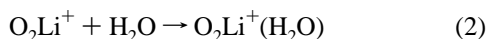
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Abstract: *Ab initio* molecular orbital calculations at the QCISD(FULL)/DZ+P level of theory were carried out on the hydrogen trioxides H₂O₃ and H₂O/O₂ (O₂ is ³Σ_g⁻) and their Li⁺ ion and proton adducts to determine the binding energies (Li⁺ affinity and proton affinity) for H₂O₃-Li⁺ and H₂O-Li⁺-O₂. Calculations include the thermochemistry at 298 K and enthalpy corrections for comparison with experimental values. Our prediction for the binding energy of Li⁺ to H₂O₃ is 33.0 kcal/mol, which closely resembles that between Li⁺ and homologous molecules of water and H₂O₂. In the case of the H₂O-Li⁺-O₂ system, the process may be that a primary product of H₂OLi⁺ would then bind to oxygen (or O₂Li⁺ to water). Binding energies of H₂OLi⁺ or Li⁺ to O₂ are 8.6 or 5.2 kcal/mol, respectively, which are smaller than those required for adduct formation under conventional experimental conditions. The overall results suggest the validity of our recent experimental detections of Li⁺ ion attachment to hydrogen trioxide. But the detection of the H₂O-Li⁺-O₂ complex may not be possible.

Introduction

Analysis by Li⁺ ion attachment mass spectrometry of products in the microwave discharge of an 80% CH₄:20% O₂ mixture¹⁻³ brought forth the unexpected observation of the *m/z* 57 peak, indicating the presence of a H₂O₃ compound. Studies were done in terms of discharge conditions with the view to increasing production rates and confirming the possible presence of this H₂O₃ compound in the gas phase with its adduct ions (H₂O₃-Li⁺) detected by mass spectrometry.⁴ Formation mechanisms were postulated⁵⁻⁹ in which the reaction of OH + HO₂ proceeds via the formation of vibrationally/rotationally excited trioxide intermediates H₂O₃*.

Another explanation for the peak at *m/z* 57 would be the adduct ion of Li⁺ with H₂O and O₂. We can expect that a primary product of O₂Li⁺ would then bind to water, or that H₂OLi⁺ would bind to oxygen.



The production rate of the Li⁺ adduct depends on the strength of the Li⁺ affinity, which is heavily dependent on the polarity or the polarizability of the target species. In other words, the chemical species captures the Li⁺ ions and yields the Li⁺ adduct if the Li⁺ affinities are sufficiently high. Under our experi-

mental conditions for Li⁺ ion attachment mass spectrometry,¹⁻³ compounds whose Li⁺ affinities are weaker than ca. 10 kcal/mol are hardly detected even if they are present in abundance.

Almost nothing was previously known about cation adducts of H₂O₃ and H₂O/O₂ or the nature of their bonding. Oxygen and hydrogen trioxides may behave characteristically, in terms of interaction with Li⁺, but they cannot be accessed experimentally. In this sense, *ab initio* molecular orbital calculations help by providing important insight into factors such as binding energies, charge distributions, geometrical distortions, and the intrinsic interaction between a compound and the Li⁺ ion.¹⁰⁻¹³

We studied lithiated species, but it is useful to extend the conditions of the present system to the interactions of protons¹⁴ for the following reasons: (i) a general understanding of complex formation can be gained by comparing and contrasting the properties of the H⁺ and Li⁺ complexes of these target systems and (ii) because the interactions of protons are of fundamental importance in chemistry and a wealth of data on proton affinity (PA) has been collected,¹⁵ while few studies of Li⁺ affinity (LA)¹⁶ are available.

This paper reports the interactions of protons and Li⁺ with H₂O₃ or H₂O/O₂. Specific topics covered here include (i) equilibrium structure, (ii) the inversion barrier in H₂O₃Li⁺, (iii) Li⁺ and H⁺ affinities of H₂O₃, (iv) interactions of H₂OLi⁺ with O₂ and O₂Li⁺ with H₂O, and (v) the nature of the bonding of Li⁺ with H₂O₃ or H₂O/O₂. The objective is to give some guide to the interpretation of (i) experimental topics on lithium ion

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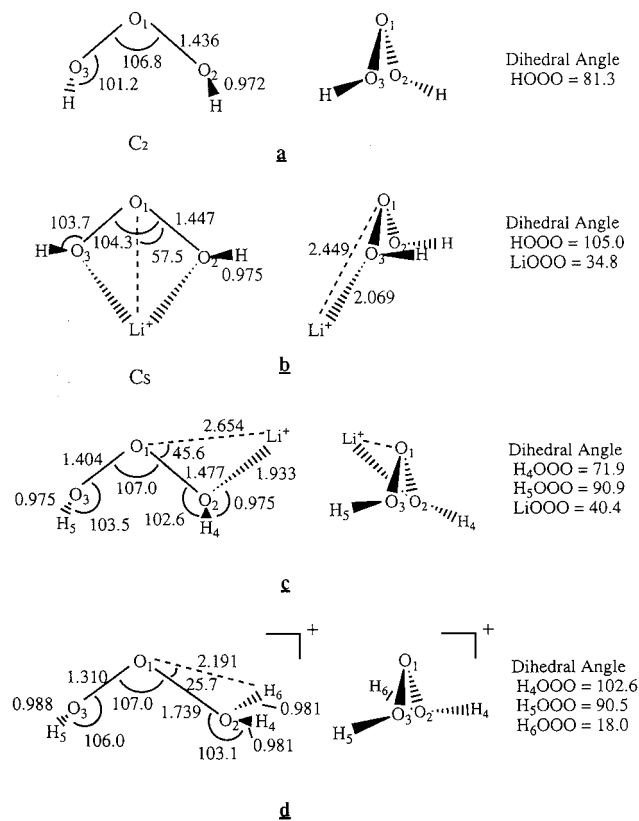


Figure 1. Molecular structures of hydrogen trioxide (a) and its Li⁺ complexes (b and c) and H⁺ complexes (d). HOOO is the dihedral angle formed by the OOO and HOO planes. Distances are given in angstroms and angles in degrees.

attachment to the H₂O₃ species in the gas phase, (ii) related topics on the calculations of H₂O₃Li⁺ interactions with oxygen molecules or O₂Li⁺ interactions with water molecules, and (iii) the differences between the Li⁺-H₂O₃ and H₂O-Li⁺-O₂ adducts. We believe that determination of Li⁺ affinity of H₂O₃ will be essential in the future development of the Li⁺ ion attachment/mass spectrometry technique for H₂O₃ detection.

Computational Details

Considering the difficulties in obtaining the Li⁺-H₂O₃ binding energies experimentally and the significance of establishing absolute binding energies, we examined the binding energies of Li⁺ to H₂O₃ and H₂O/O₂ complexes using *ab initio* molecular orbital theory including electron correlation. We calculated the structures and energies of the H₂O₃ and Li⁺ ion, together with their adducts, at a uniform level of theory. The methods used are essentially the same as those which have recently appeared in theoretical studies on computation of the total energies of molecules at their equilibrium geometries.¹⁷⁻¹⁹

All calculations were performed within the framework of the Gaussian 94 system²⁰ by using the basis sets incorporated in this system to calculate an equilibrium structure and the total energy *E*. The complete set of chemical species studied in this work is presented in Figures 1, 2, and 3, which show those lithiated (and protonated) species found to be stable or to have stationary points.

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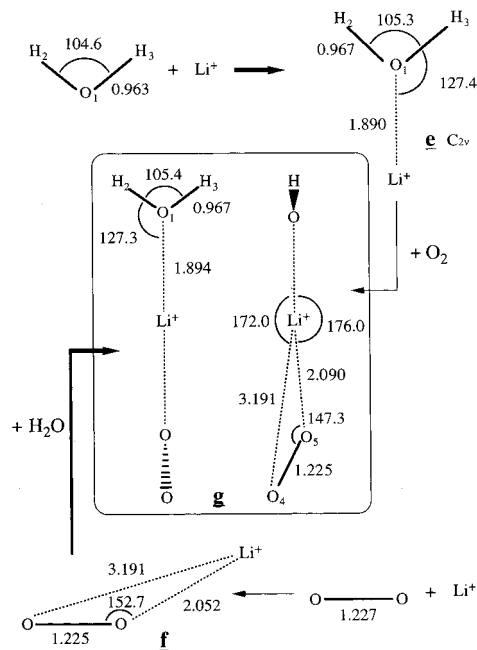


Figure 2. The production process of the Li⁺ complexes of H₂O and O₂ and their notations. Distances are given in angstroms and angles in degrees.

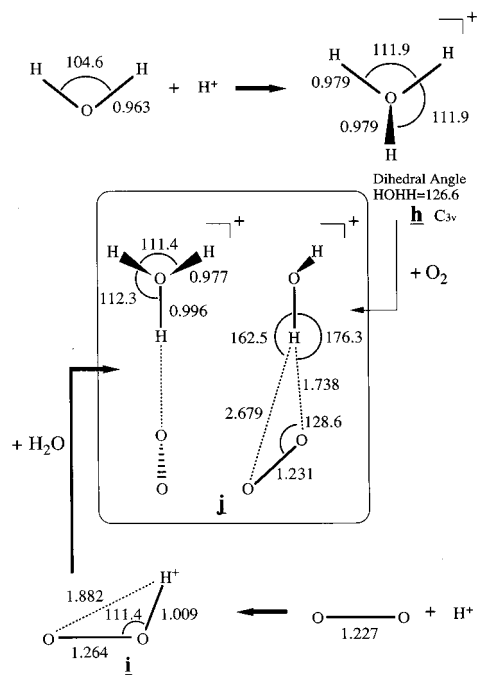


Figure 3. The production process of the H⁺ complexes of H₂O and O₂ and their notations. Distances are given in angstroms and angles in degrees.

The standard double- ζ plus polarization (DZ+P) basis sets²¹ were employed in the calculation, and consideration of core electrons was made. The geometries were optimized by the Møller-Plesset (MP2) and quadratic configuration interaction including single and double (QCISD) correlated wave functions, using energy gradient techniques. Harmonic frequency analysis with use of analytical second derivatives was carried out at the various levels at a stationary point to confirm the equilibrium structure and to provide zero-point vibrational energy (ZPE) corrections. In analyzing the site-specificity of Li⁺ addition to both H₂O₃ and H₂O/O₂, the lowest total energies of all the isomeric ions formed in these reactions were sought.

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For Li^+ affinity (and proton affinity), we employed the optimized geometry of all species involved in the reaction. The reaction enthalpy differences,

$$\Delta H^{298}(\text{Li}^+ \text{ affinity}) = \Delta E^{298} + \Delta(\text{PV}) \quad (3)$$

can be taken as a measure of the corresponding Li^+ (or H^+) affinity.

We have performed calculations on related systems where experimental data are available. The comparison shown in the Table 1 reveals that the QCISD(FULL)/DZ+P calculations provide accurate complex energies in less than $\pm 3\%$ error. For the calculations of $\text{H}_2\text{O}/\text{Li}^+$ and $\text{H}_2\text{O}/\text{H}^+$ species, the counterpoise method to estimate possible basis set superposition errors was examined. However, this additional approach makes only a very slight difference in energy. Therefore, we have not made this effort in the present study.

We computed the electrostatic potential patterns^{22,23} of the H_2O_3 molecule with the Gaussian 94 and MEPMAP²⁴ programs. These programs have the capability of searching for the Li^+ (or H^+) site that is favorable for a given molecule.

Results and Discussion

1. Geometry. All calculated geometries, which were re-optimized for a global minimum at the QCISD level with the DZ+P basis set, are given in Figure 1 (H_2O_3), Figure 2 ($\text{H}_2\text{OLi}^+\text{O}_2$), and Figure 3 ($\text{H}_2\text{OH}^+\text{O}_2$) to show the changes involved in complexation. A structural description of each species and complex at the QCISD level is given and compared with that from the literature.

(a) H_2O_3 . Many reports have been published previously,^{5,6,25} but for comparative purposes, a brief description is given here. The equilibrium conformation of H_2O_3 (a in Figure 1) has the two OH bonds directed on opposite sides of the $\text{O}_2\text{O}_1\text{O}_3$ plane in the trans form (C_2 symmetry). The geometries obtained at the QCISD level have been compared with those from the literature at the MP2/6-31G* level.²⁵ MP2 makes little difference to the equilibrium bond angles or lengths, but the dihedral angle at MP2, Φ_{HOOO} , is reported to be 78.1° , showing a slight difference to the angle of 81.3° calculated at the QCISD level, which is quite consistent with the CASSCF studies.⁶

(b) $\text{H}_2\text{O}_3\text{Li}^+$. Addition of Li^+ to H_2O_3 can occur at many different positions. The most stable form has the structure *b*, having C_s symmetry, with the Li^+ ion located symmetrically between the two oxygen atoms (O_2 and O_3). The biggest change is that the H_2O_3 fragment then becomes a cis-type arrangement.

The second isomer has the structure *c*, with the H_2O_3 fragment essentially the same as H_2O_3 . The lithium cation does not take up a symmetric position on the 2-fold axis of H_2O_3 , and the length O_3O_1 is slightly shortened to 1.403 Å, while O_1O_2 is lengthened slightly to 1.476 Å. This form, corresponding to C_1 symmetry, is 6.3 kcal/mol less stable than the C_s alternative above.

(c) $\text{H}_2\text{O}_3\text{H}^+$. As in the case of $\text{H}_2\text{O}_3\text{Li}^+$, there is no available experimental geometry for the $\text{H}_2\text{O}_3\text{H}^+$ complex. Structure *d*, which gives the global minimum, is not analogous to that of structure *b* found for $\text{H}_2\text{O}_3\text{Li}^+$. The H_2O_3 fragment remains in a trans-type arrangement, but again the structure of H_2O_3 is perturbed upon complexation with the proton, and there is significant change in the O_1O_2 and O_1O_3 lengths.

Comparisons with the $\text{H}_2\text{O}_3\text{Li}^+$ complex reveal the following: (i) the most stable structure of $\text{H}_2\text{O}_3\text{Li}^+$ has C_s symmetry in the cis form, while H^+ is located close to one oxygen atom (O_2 or O_3); (ii) as expected, the $\text{O}-\text{H}^+$ length (0.980 Å) in structure *d* is significantly shorter than the $\text{O}-\text{Li}^+$ length (2.437 Å) for the $\text{H}_2\text{O}_3\text{Li}^+$ cation *b* and (iii) the O_1O_2 length has increased greatly in the protonated form, and the structure in Figure 1d is taking on the appearance of H_2O and HO_2 moieties sharing a positive charge, which is very different from the lithiated form.

(d) $\text{H}_2\text{OLi}^+\text{O}_2$ and $\text{H}_2\text{OH}^+\text{O}_2$. The production process of the Li^+ complexes and H^+ complexes of $\text{H}_2\text{O}/\text{O}_2$ and their notations are schematically shown in Figures 2 and 3. For comparative purposes, structural data for the Li^+ and H^+ complexes of H_2O and O_2 are also given, together with those of $\text{H}_2\text{O}/\text{O}_2$.

Many reports on H_2OLi^+ and H_2OH^+ have been published previously.¹² Briefly, in H_2OLi^+ the lithium cation is attached to water along the dipole axis, leaving the overall symmetry unchanged. The H_2OLi^+ is planar in its ground state (C_{2v} structure, see e in Figure 2). The structural features with complex formation are that (i) H_2OLi^+ remains planar C_{2v} and (ii) the $\text{H}_2\text{O}_1\text{H}_3$ angle opens out and the H_2O_1 length increases slightly. This contrasts with the extensively studied H_2OH^+ that becomes pyramidal at HF/6-31G*.²⁶ The pyramidal structure, h, of H_2OH^+ , which is confirmed also by the present calculations at QCISD/DZ+P, is in agreement with experimental data.²⁷

O_2Li^+ is found to have the bent structure²⁸ of C_s symmetry with an OOLi^+ angle of 152.7° . The $\text{O}-\text{Li}^+$ distance is comparatively long, and a slight decrease (0.001 Å) of the $\text{O}-\text{O}$ distance is found on lithiation. The association energy is relatively weak (5.2 kcal/mol). These results are not comparable to those for N_2 molecules,²⁹ as N_2Li^+ has a linear structure with a bond length little changed from that of N_2 .¹² However, the $\text{N}-\text{Li}^+$ distance (2.61 Å) is also comparatively long and the association energy relatively weak (12.0 kcal/mol).

$\text{H}_2\text{OLi}^+\text{O}_2$ has a C_1 structure with three bonds at the Li^+ ions. Again, this interaction would favor a geometry in which the Li^+ ion is not along the symmetrical axis of the molecule. The Li^+-O_1 distance is 1.883 Å, whereas those of Li^+-O_4 and Li^+-O_5 are 3.221 and 2.073 Å, respectively. The optimal geometries of the H_2OLi^+ and O_2Li^+ fragments of the complex $\text{H}_2\text{OLi}^+\text{O}_2$ (g) are very similar to those found in H_2OLi^+ (e) and Li^+O_2 (f).

The complex $\text{H}_2\text{OH}^+\text{O}_2$ (j) is similar to the corresponding lithiated complexes. However, the presence of H^+ does appreciably decrease some of the intermolecular distances.

2. Inversion Barrier in $\text{H}_2\text{O}_3\text{Li}^+$. The calculations leave little room for doubt in concluding that $\text{H}_2\text{O}_3\text{Li}^+$ has a C_s equilibrium geometry in a cis-type arrangement. The optimized structures for the transition state (TS) to the global minimum point on the $\text{H}_2\text{O}_3\text{Li}^+$ potential energy surface and its transition vectors as determined by a numerical frequency calculation at the QCISD level are shown in Figure 4. The harmonic mode associated with the single imaginary frequency is consistent with this inversion process, with migration, primarily by H atoms, indicated by the transition vectors.

Though the HF, MP2, and QCISD geometries (C_2) for the transition state are qualitatively the same, there are some

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Table 1. The Protonation (PA) and Lithiation (LA) Energy^a of the H₂O₃ and H₂O/O₂ Molecules and Inversion Barrier of H₂O₃Li⁺, in kcal/mol

inversion barrier	HF/DZ+P	MP2(FULL)/DZ+P	QCISD(FULL)/DZ+P	literature	
				theor	exptl
H ₂ O ₃ Li ⁺	0.4	0.9	0.9		
PA(H ₂ O ₃)	158.5	164.1	160.8		
LA(H ₂ O ₃)	31.0	33.6	33.0		
PA(H ₂ O)	169.4	168.4	169.7	173.3 ^b	173.0
LA(H ₂ O)	35.2	34.7	34.5	39.0 ^b	34.0
PA(O ₂)	107.0	94.0	103.0		100.4
LA(O ₂)	7.7	3.3	5.2	5.0 ^c	
H ₂ OH ⁺ affinity(O ₂)	3.9	2.5	3.3		
O ₂ H ⁺ affinity(H ₂ O)	66.3	76.8	70.0		
H ₂ OLi ⁺ affinity(O ₂)	6.9	7.2	8.6		
O ₂ Li ⁺ affinity(H ₂ O)	34.4	38.5	37.9		

^a Both protonation and lithiation energies are given in enthalpy difference, $\Delta H^{298} = \Delta E^{298} + \Delta(PV)$. ^b From the MP2/6-31G* studies (ref 11). ^c From the MP4/6-31G* studies (ref 27).

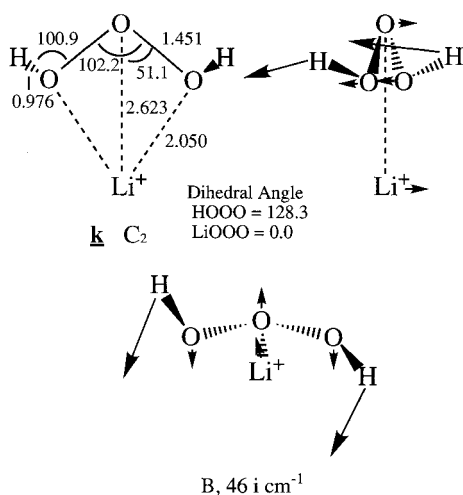


Figure 4. Calculated QCISD geometries of H₂O₃Li⁺ for the transition state to inversion. The transition vectors are also shown in the transition state, together with the imaginary frequency. Distances are given in angstroms and angles in degrees.

differences between them. The theoretical inversion barrier (relative energies) is also shown for H₂O₃Li⁺ in Table 1. Comparing the results for C₂ (k) and C_s (b) energies, H₂O₃Li⁺ has a very small barrier height, estimated as being 0.4 kcal/mol at the HF level. The QCISD electron correlation contributes substantially to the inversion barrier; the QCISD inversion barrier is higher than that of HF, whereas the effects of MP2 and QCISD are almost identical. The positive contribution (0.5 kcal/mol) of the QCISD electron correlation to the inversion barrier in H₂O₃Li⁺ is similar to values reported previously for H₂OH⁺.²⁶

3. Proton and Li⁺ Affinity of H₂O₃. The Li⁺–H₂O₃ adducts, as well as protonated H₂O₃, have been little studied. The bond strengths of these species are of interest, particularly when associated with their possible observation by mass spectrometry. With regard to H⁺ and Li⁺ affinities, total energies (E_0^{298} , in atomic units) with inclusion of the zero-point energy (ZPE) and the thermal energy corrections (at 298.15 K) are provided as Supporting Information. We computed the thermochemistry at 298.15 K and the enthalpy correction as $-RT$ to compare the experimental values (Table 1).

(a) Proton affinity of H₂O₃. Analysis of the electrostatic potentials suggests that the presence of H⁺ tends to stabilize the complex with the bond formed (structure d), leading to a strong bond. The protonation energy of H₂O₃ is 169.7 kcal/mol at the QCISD/DZ+P level, which is quite stable with

respect to dissociation. Thus, the H₂O₃H⁺ complexes should be observable mass spectrometrically, if experimental techniques are devised to permit proton transfer reactions in the gas phase.

(b) Li⁺ affinity of H₂O₃. Li⁺ also interacts with the oxygen atoms. The lithiation energy (Li⁺ affinity) with the three bonds formed at Li⁺ (structure b) is calculated to be 33.0 kcal/mol, which is 6.3 kcal/mol stronger than that formed as structure c. Again the H₂O₃Li⁺ adducts are stable with respect to dissociation and are thus observable mass spectrometrically.

The values of Li⁺ affinity presently calculated for H₂O₃ are slightly weaker than those calculated for water and H₂O₂ systems—the Li⁺ affinities at the QCISD level are 37.2 kcal/mol for water (37.21 kcal/mol reported at the MP2/6-31G* level¹¹), and 36.0 kcal/mol for H₂O₂ (34.26 kcal/mol at the MP2/6-31G* level¹¹).

4. Interactions of H₂OLi⁺ with O₂ and O₂Li⁺ with H₂O.

Before studying the binding energies of H₂OLi⁺ with O₂ and O₂Li⁺ with H₂O, we calculated the PA and Li⁺ affinity of H₂O and O₂, again at the QCISD/DZ+P level, and the results are directly compared to previously reported values. A summary is shown also in Table 1, together with the interactions of H₂O₃ and H₂O/O₂ with Li⁺ ions and protons.

Reports on H₂OLi⁺ and H₂OH⁺ have been published previously¹² and, as expected, the present PA and Li⁺ affinities (LA) of H₂O are in good agreement with available experimental values from Beauchamp's measurements³⁰ and theoretical values at the HF/6-31G* level.¹¹ However, cation–oxygen adducts have not been studied at all. The PA and LA of oxygen presented in this study are 103.0 and 5.2 kcal/mol, respectively. The calculated PA (O₂) differs from the experimental values by only 2.6 kcal/mol.

The electronic ground-state potential surface of H₂OLi⁺O₂ has the global minimum for a C₁ structure (g). The binding energy of H₂OLi⁺ with O₂ is calculated to be 8.6 kcal/mol, which is weaker than that required for H₂OLi⁺O₂ formation under our experimental conditions. On the other hand, the present calculations predict that the O₂Li⁺ affinity of H₂O of O₂Li⁺–H₂O in a C₁ conformation is 37.9 kcal/mol and hence we can reasonably predict that the complexes should be easily produced when O₂Li⁺ is present. But that is not the case in our experiments, and hence the H₂OLi⁺O₂ may not be detectable (or the O₂Li⁺ is not present).

5. Concluding Remarks. With regards to the Li⁺ affinity of H₂O₃ and H₂O/O₂, which we were unable to obtain experimentally, the following concluding remarks can be drawn

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from this study of the structures and energies of H_2O_3 , $\text{H}_2\text{O}_3\text{-Li}^+$, $\text{H}_2\text{OLi}^+\text{-O}_2$, and $\text{O}_2\text{Li}^+\text{-H}_2\text{O}$, using *ab initio* molecular orbital theory including correlation effects:

1. The Li^+ affinity of H_2O_3 is calculated to be 33.0 kcal/mol at the QCISD/DZ+P level. This is comparable to other Li^+ affinities of homologous molecules, H_2O_2 and H_2O . However, this value is still large enough for H_2O_3 to be attached to Li^+ ions and hence the Li^+ adducts of H_2O_3 should be observable mass spectrometrically.

2. Regarding the system of $\text{H}_2\text{O/O}_2$, the binding energies of $\text{O}_2\text{-Li}^+$, $\text{H}_2\text{OLi}^+\text{-O}_2$, and $\text{O}_2\text{Li}^+\text{-H}_2\text{O}$ are calculated as 5.2, 8.6, and 37.9 kcal/mol, respectively. Clearly O_2 has weak Li^+ and H_2OLi^+ affinities and is not easily attached to either Li^+ or H_2OLi^+ ions. Therefore, $\text{H}_2\text{OLi}^+\text{O}_2$ may not be observable with our Li^+ ion attachment mass spectrometric system.

3. The nature of bonding is evaluated by using Mulliken population analysis. There is a small charge transfer in lithiated species because of the electropositive nature of the alkali metal; i.e., Li^+ retains 0.86 electronic units (e) of its positive charge in the $\text{H}_2\text{O}_3\text{Li}^+$ adducts, demonstrating that bonding is due mostly to electrostatic interaction, the main contribution of which is made by the ion–dipole attractions. On the other hand, the determining factor for relative stabilities in the case of the protonated H_2O_3 is the charge transfer character, i.e. the favorable electron delocalization (at least 0.44 e in the adduct products).

4. The Li^+ attachment sites toward O_2 and $\text{H}_2\text{O/O}_2$, which are not located on any symmetrical axis of the molecular species, are interesting. This asymmetry, which may be associated with the Renner–Teller effect,³¹ has not been considered in the present report.

A final note: The lifetimes of $\text{Li}^+\text{H}_2\text{O}_3$ are satisfactorily long enough to be detected, since fragmentation can be assumed to be negligible in the Li^+ ion attachment mass spectrometry.³²

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Supporting Information Available: Table giving the total energies E_0^{298} with electron correlation in atomic units, calculated at the HF/DZ+P, MP2(FULL)/DZ+P and QCISD(FULL)/DZ+P levels (1 page). See any current masthead page for ordering and Internet access instructions.

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