# Conformational Stability of the Propylene Oxide−Water Adduct: Direct Spectroscopic Detection of O−H···O Hydrogen Bonded Conformers

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***Abstract:*** The 1:1 molecular adduct of propylene oxide and water (PO−$H_2O$) was studied using Fourier transform microwave spectroscopy and high level ab initio methods. Two distinct structural conformers with the water molecule acting as a proton donor were detected experimentally: one with the water on the same side as the methyl group with respect to the ether ring, i.e., *syn*-PO−$H_2O$, the other with the water molecule binding to the O-atom from the opposite side of the methyl group, i.e., *anti*-PO−$H_2O$. The nonbonded hydrogen is *entgegen* to the ether ring in both conformers. Rotational spectra of four isotopic species, namely PO−$H_2O$, PO−DOH, PO−HOD, and PO−$D_2O$, were recorded for the two conformers. The hydrogen bond parameters: $r(O_{epoxy}···H)$, $\angle(ring-O_{epoxy}···H)$, and $\angle(O_{epoxy}···H-O)$ are 1.908 Å, 112°, and 177° for *syn*-PO−$H_2O$, and 1.885 Å, 104.3°, and 161.7° for *anti*-PO−$H_2O$, respectively. The experimental results suggest that the hydrogen bond in *syn*-PO−$H_2O$ is stronger and the monomer subunits are more rigidly locked in their positions than in the ethylene oxide-water adduct. The stabilizing effect of the methyl group to the intermolecular hydrogen bond is discussed in terms of the experimentally estimated binding energies, the structural parameters, and the ab initio calculations.

## Introduction

An understanding of the intermolecular interactions involving chiral molecules on the molecular level is of great importance in life sciences. In particular, the interactions between water and chiral molecules are of significant interest since hydrogen bonding governs the solvation processes in the aqueous environments.[1] In recent years, jet-cooled high resolution spectroscopy has been successfully applied to study a number of water-organic molecule adducts[2] such as benzene-water,[3] phenol-water,[4] ethylene oxide (EO)-water,[5] oxetane-water,[6] and tetrahydrothiophene-water.[7] These studies provided detailed and precise information about the structures and dynamics of these hydrogen bonded systems. On the other hand, there exist only a very small number of rotationally resolved spectroscopic publications on water-chiral molecule adducts.[8,9] The studies of water-chiral

molecule complexes are complicated by the large number of potential structural conformers and the involved spectral pattern since chiral molecules have no symmetry. Therefore, size and conformational flexibility of the concerned chiral molecule need to be considered if attempting experimental and high level ab initio studies.

In this work, we report detailed rotational spectroscopic and ab initio computational studies of the hydrogen bonded propylene oxide (PO)−water complex. PO is one of the smallest, rigid, and chemically stable chiral molecules that can be regarded as truly "organic". It has one chiral center, namely the carbon atom bonded with the methyl group. Only one enantiomeric form of PO is of significance here. We use the *S*-form throughout this paper and therefore drop this additional notation for simplicity. Although the PO monomer was investigated with rotational spectroscopy a long time ago,[10−12] the van der Waals complexes of PO−rare gas (rare gas = Ne,[13,14] Ar,[15] Kr[16]) were the only PO containing complexes studied so far using high resolution spectroscopy. The correct identifications of the lowest energy structures of these complexes were only achieved through a detailed comparison between the theoretical and experimental

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results.[13,16] This underscores the challenges associated with spectroscopic characterizations of molecular complexes containing chiral molecules.

In this article, we focus our attention on the $O_{epoxy}\cdots H-O$ type hydrogen bond and the effect of the additional interaction between the methyl group and $H_2O$ on the stability of the potential structural conformers. Very recently, the role of the methyl groups in the formation of hydrogen bond in dimethyl sulfoxide−methanol mixtures was studied using attenuated total reflection Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and ab initio methods.[17] A stabilizing contribution of the methyl groups to the intermolecular hydrogen bond through charge transfer was reported. Closely related to the current investigation are a number of rotationally resolved spectroscopic studies of ether−water complexes such as EO−water,[5] 1,4-Dioxane−water,[18] and tetrahydropyran−water,[19] conducted by Caminati and co-workers using a pulsed jet millimeterwave spectrometer and a Fourier transform microwave spectrometer. In all these cases, only the lowest energy conformer could be detected experimentally. High-resolution spectroscopy of the PO−water adduct provides us with the opportunity to probe the possible conformers in great detail and to examine the effect of the methyl group on the stability of the $O_{epoxy}\cdots H-O$ type hydrogen bond by comparing them with the closely related EO−water adduct.[5]

**Ab Initio Calculations**

In terms of a conventional hydrogen bond, PO can only act as a proton acceptor. On the basis of chemical intuition and the experimental results of other ether-water complexes,[5,18,19] one may expect PO−$H_2O$ to form an $O_{epoxy}\cdots H-O$ hydrogen bond with the possibility of the water molecule lying on either side of the ether ring to interact with the lone electron pairs of the oxygen atom. To assist the spectral search and assignment, we carried out complete geometry optimizations using the GAUSSIAN03[20] software package at the level of second-order Møller−Plesset perturbation theory[21] (MP2) with the following basis sets: 6-311++G(d,p),[22] cc-pVDZ,[23] and aug-cc-pVDZ.[24] Two minimum energy configurations, namely, *syn*-PO−$H_2O$, i.e., $H_2O$ on the same side of the ring as the methyl group, and *anti*-PO−$H_2O$, i.e., $H_2O$ approaching PO from the opposite direction of the methyl group with respect to the ether ring, were found with all three basis sets. Their minimum nature was confirmed by the absence of imaginary frequencies in the harmonic frequency calculations. In addition, geometry optimizations were also performed for the *entgegen* and *zusammen* positions[5] of the nonbonded water hydrogen with respect to the ether ring. For both *syn*- and *anti*-configurations, the *zusammen* form always converges to the *entgegen* orientation during the geometry optimization procedures. In the study of EO−$H_2O$, the *entgegen* form was calculated to be a local minimum in
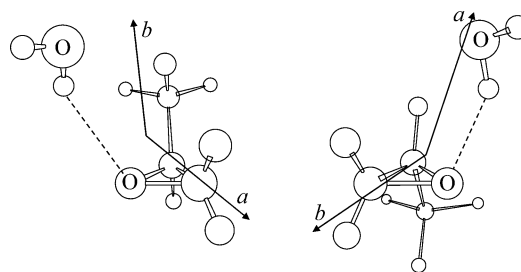


**Figure 1.** Optimized geometries of the *syn*-PO−$H_2O$ (left) and *anti*-PO−$H_2O$ (right) conformers at the MP2/6-311++G(d,p) level of theory in their respective principal axis systems. The unlabeled elements are H and C atoms.

**Table 1.** Calculated Dissociation Energies, Counterpoise (CP) Corrections for the Basis Set Superposition Errors, and Zero-Point Vibrational Energy (ΔZPE) Corrections in Units of kJ/mol for the Two Conformers of the PO−$H_2O$ Complex and the EO−$H_2O$ Complex at the MP2/6-311++G(d,p) Level of Theory

|  | *syn*-PO–$H_2O$ | *anti*-PO–$H_2O$ | EO–$H_2O$ |
|---|---|---|---|
| $D_e$ | -29.89 | -29.80 | -28.99 |
| CP | 7.02 | 6.80 | 6.83 |
| ΔZPE | 8.18 | 8.20 | 8.54 |
| $D_0 = (D_e + \Delta ZPE)$ | -21.71 | -21.60 | -20.45 |
| $D_0 + 50\%$CP | -18.20 | -18.20 | -17.04 |

agreement with the experimental finding, while the *zusammen* form was found to be a saddle point that is 6.7 kJ/mol higher in energy than the *entgegen* form.[5] It is interesting to note that this preference already shows up in the EO−$H_2O$, 1,4-Dioxane-$H_2O$, and tetrahydropyran-$H_2O$ complexes, by considering just the dipole−dipole interaction.[5] Based on the MP2/6-311++G-(d,p) geometries, we calculated the dipole−dipole interaction energies for the *entgegen* and *zusammen* forms of PO−$H_2O$. For *anti*-PO−$H_2O$, the dipole−dipole interaction favors the *entgegen* form over the *zusammen* form by 1.8 kJ/mol, just as in the cases of the other three ether-water complexes discussed above. For *syn*-PO−$H_2O$, however, the opposite was found: the *zusammen* form is more stable, by 1 kJ/mol, than the *entgegen* form when only dipole−dipole interaction energies were considered. One plausible explanation for this behavior is the steric hindrance effect of the methyl group in *syn*-PO−$H_2O$ that prevents the dipole moments of the two subunits to orient in a similar fashion as in EO−$H_2O$ or in *anti*-PO−$H_2O$. The preference for the *entgegen* form in *syn*-PO−$H_2O$ is therefore caused by other factors such as the additional secondary hydrogen bonds between the methyl group and $H_2O$, as discussed in the later section.

The MP2/6-311++G** optimized structures of the complexes are shown in Figure 1 in their respective principal inertial axis systems. The binding energies calculated with MP2/6-311++G** for the *syn*- and *anti*-configurations are listed in Table 1. Also included in Table 1 are the basis set superposition errors (BSSE) calculated with the counterpoise correction method[25] and the zero-point vibrational energy corrections for these two configurations. It has been shown that a complete basis set extrapolation gives a binding energy that is always bracketed by the BSSE corrected and uncorrected values.[26] In the previous ab initio investigation of the propylene imine-$H_2O_2$

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**Table 2.** Predicted Rotational Constants and Dipole Moment Components of the Two Conformers of the PO–$H_2O$ Complex at the MP2/6-311++G(d,p) Level of Theory

|  | syn-PO–$H_2O$ | anti-PO–$H_2O$ |
|---|---|---|
| $A$ /MHz | 6047.94 | 9488.04 |
| $B$ /MHZ | 3082.87 | 2310.28 |
| $C$ /MHz | 2385.19 | 2112.86 |
| $\mu_a$ /D | 2.04 | 1.79 |
| $\mu_b$ /D | 0.25 | 0.29 |
| $\mu_c$ /D | 0.06 | 0.08 |

**Table 3.** Experimental Transition Frequencies (MHz) of the syn-PO–$H_2O$ and anti-PO–$H_2O$ Conformers

| $J_{KaKc} - J'_{Ka'Kc'}$ | syn-PO–$H_2O$ | anti-PO–$H_2O$ |
|---|---|---|
| $1_{01} - 0_{00}$ | 5388.4336 (16)[a] | 4362.0899 (44) |
| $1_{10} - 1_{01}$ |  | 7398.3921 (60) |
| $1_{11} - 0_{00}$ | 8415.9695 (−19) | 11559.4636 (61) |
| $1_{10} - 0_{00}$ | 9098.9856 (−12) |  |
| $2_{02} - 1_{01}$ | 10673.6683 (10) | 8719.8967 (26) |
| $2_{11} - 1_{10}$ | 11459.5264 (−30) | 8925.1946 (26) |
| $2_{12} - 1_{11}$ | 10093.5815 (26) | 8523.2116 (−9) |
| $2_{11} - 2_{02}$ |  | 7603.6870 (29) |
| $2_{12} - 1_{01}$ | 13121.1188 (5) | 15720.5913 (68) |
| $2_{11} - 1_{01}$ | 15170.0844 (3) | 16323.5780 (−2) |
| $3_{21} - 2_{20}$ | 16561.2025 (−5) | 13103.2601 (32) |
| $3_{03} - 2_{02}$ | 15767.1860 (9) | 13069.1687 (23) |
| $3_{12} - 2_{11}$ | 17118.8105 (−12) | 13384.7918 (−4) |
| $3_{13} - 2_{12}$ | 15079.9261 (10) | 12781.9920 (−56) |
| $3_{22} - 2_{21}$ | 16163.7808 (−5) | 13086.7248 (35) |
| $3_{12} - 3_{03}$ | 5848.0459 (25) | 7919.3155 (56) |
| $3_{21} - 3_{12}$ | 8628.6532 (0) |  |
| $4_{04} - 3_{03}$ |  | 17405.7149 (16) |
| $4_{13} - 3_{12}$ |  | 17840.7196 (72) |
| $4_{14} - 3_{13}$ |  | 17037.4728 (19) |
| $4_{04} - 3_{13}$ |  | 10692.1989 (72) |

[a] The residuals (obs-calc) in parentheses in units of the last digits.

adduct,[27] we found that the BSSE tends to overcorrect the binding energies with small basis sets and that an empirical 50% BSSE correction gives a better estimate of the dissociation energies. Therefore, a 50% BSSE correction was also used here. The calculated results for EO–water are also listed in Table 1 for comparison. While the uncorrected binding energy for *syn*-PO–$H_2O$ is 7.5 $cm^{-1}$ more than that of *anti*-PO–$H_2O$, the final corrected binding energies are the same for the two conformers. Therefore, we do not know a priori which conformer is more stable and will be observed experimentally. Both conformers of the PO–water adduct are predicted to be more strongly bound than the EO–water complex.

The MP2/6-311++G** rotational constants and dipole moment components for the normal isotopomers of the two PO–$H_2O$ conformers are given in Table 2. The *anti*-configuration was predicted to be a near prolate top with $\kappa = -0.946$, while the *syn*-configuration is a fairly asymmetric top with $\kappa = -0.619$. The large difference between the two sets of rotational constants suggests distinguishable spectral pattern for the two configurations. The prominent dipole moment component lies along the *a*-axis and the magnitudes of the *b*- and *c*- dipole moments were predicted to be considerably smaller for both conformers with all three basis sets. The detailed results from the ab initio calculations with all three basis sets and for the deuterated species are summarized in Table S1, available as Supporting Information.

**Experimental Section**

A molecular beam Fourier transform microwave spectrometer,[28] operated in the frequency region between 4 and 26 GHz, was used in this study. The estimated uncertainty of the frequency measurements for the well resolved peaks is ±1 kHz. At room temperature, a gas mixture of 0.14% $H_2O$ and 0.14% PO (99+%, Aldrich) in 5 bar neon (Praxair) was expanded through a pulsed pinhole nozzle (General Valve Series 9). The effective rotational temperature in the expansion was estimated to be lower than 1 K. Isotopically enriched $D_2O$ (99.8%, Cambridge Isotope Laboratories) was used for the investigation of the $D_2O$ containing isotopomers. The spectra of the isotopomers containing partially deuterated water were obtained in the same experiments with the $D_2O$ sample because the fast proton exchange between $D_2O$ and the residual $H_2O$ in the sample reservoir produced sufficient amount of DOH after a few hours.

**Rotational Spectra**

Initial spectral searches were carried out for the strong *a*-type transitions for the normal isotopomers of both conformers based on the ab initio predictions. Rotational transitions with $J$ up to 4 and $K_a$ up to 2 were found and assigned. The initial fits with the *a*-type transitions were used to predict the much weaker *b*-

and *c*-type transitions. Indeed, a few weak *b*- and *c*-type transitions were detected. The measured rotational transition frequencies for *syn*-PO–$H_2O$ and *anti*-PO–$H_2O$ are listed in Table 3. Although no Stark measurements were carried out for these complexes, we were able to get a rough estimate for the magnitudes of the dipole moment components using the optimized microwave excitation pulse widths and the known dipole moment of OCS (0.7149 D).[29] The magnitude of the *a*-dipole moment component is about 2 D for both conformers. The magnitudes of the *b*- and *c*-dipole moment components are estimated to be in the order of one tenth of Debye with the *b*-dipole moment component being slightly larger. The above observations are in accord with the MP2/6-311++G(d,p) calculations. No splittings due to the internal rotation of the methyl group were observed for *syn*-PO–$H_2O$ or for *anti*-PO–$H_2O$. On the other hand, fairly narrow tunneling splittings of less than 2 kHz were predicted for *syn*-PO–$H_2O$ and less than 10 kHz for *anti*-PO–$H_2O$ with the XIAM internal rotation program,[30] assuming that the barrier height remains the same as in the monomer. Therefore, no concrete conclusion can be reached about the methyl internal rotation barrier height from the present study.

The searches and assignments for the other isotopomeric species followed the procedure described above. A summary of all the measured transition frequencies of the minor isotopomers are provided as Supporting Information in Table S2. Small splittings of a few to about twenty kHz were observed in a number of transitions of the D containing isotopomers. These are due to the quadrupolar deuterium nucleus/nuclei (nuclear spin quantum number $I_D = 1$). No attempt was made to analyze these hyperfine structures in detail because the splittings were only partially resolved in most cases. The transition frequencies of the most intense components were used in the rotational fits in these cases. The uncertainties in these transition frequencies were estimated to be ±5 kHz.

The measured rotational transition frequencies of all the isotopomeric species were fitted with Watson's *S*-reduction

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**Table 4.** Experimental Rotational and Centrifugal Distortion Constants of the Parent and the Deuterated Isotopomers of the *syn*-PO−H$_2$O Conformer

|  | PO−HOH | PO−DOH | PO−HOD | PO−DOD |
|---|---|---|---|---|
| $A$ /MHz | 6063.2695 (7)[a] | 6051.271 (1) | 6047.92 (4) | 6036.849 (1) |
| $B$ /MHZ | 3035.7424 (4) | 2994.1636 (7) | 2873.0355 (8) | 2837.4176 (7) |
| $C$ /MHz | 2352.7137 (4) | 2328.2062 (7) | 2254.4995 (7) | 2232.9386 (7) |
| $D_J$ /kHz | 5.99 (2) | 5.76 (2) | 4.93 (3) | 4.80 (2) |
| $D_{JK}$ /kHz | 41.52 (5) | 40.0 (2) | 39.7 (5) | 35.7 (2) |
| $D_K$ /kHz | −88.6 (2) | −88.6 (−)[b] | −88.6 (−)[b] | −88.6 (−)[b] |
| $d_1$ /kHz | −1.67 (1) | −1.66 (2) | −1.31 (2) | −1.20 (2) |
| $d_2$ /kHz | −0.594 (7) | −0.34 (4) | −0.31 (−)[c] | −0.31 (4) |
| $N^d$ | 15 | 10 | 7 | 10 |
| $\sigma$ /kHz[e] | 1.5 | 0.7 | 2.4 | 2.0 |

[a] Standard error in parentheses are expressed in units of the last digits. [b] Fixed at the corresponding value of the parent species. [c] Fixed at the corresponding value of the DOD species. [d] Number of transitions in the fit. [e] rms deviation of the fit.

**Table 5.** Experimental Rotational and Centrifugal Distortion Constants[a] of the Parent and Deuterated Isotopomers of the *anti*-PO−H$_2$O Conformer

|  | PO−HOH | PO−DOH | PO−HOD | PO−DOD |
|---|---|---|---|---|
| $A$ /MHz | 9478.8538 (4)[b] | 9446.634 (1) | 9394.77[c] | 9356.674 (1) |
| $B$ /MHZ | 2281.5644 (2) | 2248.9839(9) | 2177.438 (1) | 2149.6736 (5) |
| $C$ /MHz | 2080.5421 (2) | 2054.3828(8) | 1993.6911 (8) | 1969.9105 (4) |
| $D_J$ /kHz | 5.237 (5) | 4.954(6) | 4.67(3) | 4.253 (8) |
| $D_{JK}$ /kHz | −39.23 (3) | −36.5 (1) | −21.5 (3) | −33.7 (1) |
| $d_1$ /kHz | −1.015 (4) | −1.13 (4) | 0.01917 (4) | −0.53 (1) |
| $d_2$ /kHz | −0.270 (7) | −3.5 (9) | −0.27 (−)[d] | −0.27 (−)[d] |
| N[e] | 19 | 12 | 6 | 11 |
| $\sigma$/kHz[f] | 4.4 | 3.0 | 3.3 | 7.3 |

[a] $D_K$ was fixed at 0.0 for all isotopomers. See text for discussion. [b] Standard error in parentheses in units of the last digits. [c] Fixed at the corresponding value from the MP2/6-311++G(d,p) calculations. [d] Fixed at the corresponding value of the parent isotopomer. [e] Number of transitions in the fit. [f] rms deviation of the fit.

Hamiltonian in its $I^r$-representation.[31] The resulting spectroscopic constants are summarized in Table 4 for *syn*-PO−water and in Table 5 for *anti*-PO−water. In the case of *anti*-PO-water, there is not enough information to fit both $A$ and $D_K$ because the system is a near prolate top. Therefore, the $D_K$ values were fixed at 0.0 kHz for all the isotopomers. The standard deviations of the fits for *anti*-PO−water in Table 5 are therefore slightly larger than for *syn*-PO−water where all five quartic centrifugal distortion constants were fitted independently. Some distortion constants of the minor isotopomers had to be fixed at the corresponding values of the normal or related isotopomers due to the less extensive data available. In general, the MP2 calculations with the 6-311++G(d, p) basis sets gave the best agreement with the experimental rotational constants, with consistent deviations for all isotopomeric species of both *syn*- and *anti*-configurations. The largest deviation is about 1.5% with MP2/6-311++G(d, p), whereas the deviation is 8.5% with MP2/cc-pVDZ and 5.4% with MP2/aug-cc-pVDZ. Similar behavior has also been observed for non-hydrogen bonded van der Waals complexes, e.g., cyclopropane-CO$_2$[32] where the largest deviation is only 1.3% with MP2/6-311++G(d, p).

## Structural Analyses

To analyze the relative orientation of the two subunits in the respective structural conformers, we used the experimental

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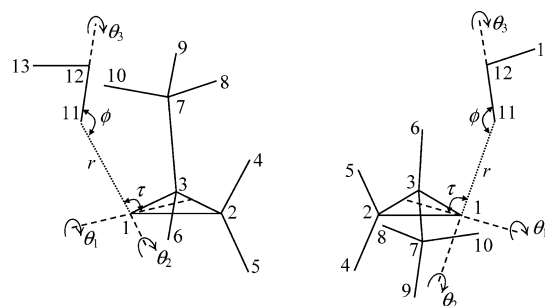
**Figure 2.** Definition of the H-bonding parameters for the *syn*-PO−H$_2$O (left) and the *anti*-PO−H$_2$O (right) conformers.

**Table 6.** Experimental and MP2/6-311++G(d,p) Hydrogen Bond Structural Parameters of the PO−H$_2$O Complex, Together with the Experimental Values of the EO−H$_2$O Complex for Comparison

|  | *syn*-PO−H$_2$O | | *anti*-PO−H$_2$O | | EO−H$_2$O[a] |
|---|---|---|---|---|---|
|  | exp. | theo. | exp. | theo. | exp. |
| $r$ /Å | 1.908 (7) | 1.905 | 1.885 (2) | 1.900 | 1.92 (1) |
| $\tau$ /deg | 110 (1) | 115.4 | 103.7 (3) | 106.7 | 103 (1) |
| $\phi$ /deg | 177 (2) | 158.2 | 161.7 (6) | 153.1 | 163 (2) |
| $\theta_1$ /deg | 80.0 (9) | 80.1 | −94.5 (4) | −89.3 | 90.0 |
| $\theta_2$ /deg | −10.0[b] | −10.0 | 51 (5) | −0.3 | 0.0 |
| $\theta_3$ /deg | −157 (9) | −168.6 | −233 (4) | −179.4 | −180.0 |
| $R_{CM}$ /Å[c] | 3.15 | 3.105 | 3.45 | 3.405 | 2.84 |
| $\angle$(ring-O$_{epoxy}$···H) /deg[c] | 112 | 117.1 | 104.3 | 106.7 | 103 |

[a] ref 5. The $\theta$ angles are fixed by the symmetry of the complex. [b] Fixed at the corresponding to theoretical value. See text for detail. [c] Calculated from the respective derived structures.

rotational constants in the structural fitting procedures. In these fits, the structures of water and PO were assumed to be unchanged upon complex formation and the experimental structural parameters for water[33] and PO[12] were used. This is a reasonable assumption since the ab initio calculations suggested little changes of the structures of the two monomers upon formation of the complex. Six additional structural parameters (defined in Figure 2) are needed to describe the relative orientations of the two monomers. These are the three parameters for the hydrogen bonded hydrogen atom of H$_2$O: $r$ (H-bond length O$_{epoxy}$···H), $\tau$ ($\angle$(C$_m$−O$_{epoxy}$···H)), and $\theta_1$ ($\angle$(C$_2$−C$_m$−O$_{epoxy}$···H)); the two parameters for the O atom: $\phi$ ($\angle$(O$_{epoxy}$···H−O)) and $\theta_2$ ($\angle$(C$_m$−O$_{epoxy}$···H−O)); and the dihedral angle $\theta_3$ ($\angle$(O$_{epoxy}$···H−O−H)) for the nonbonded hydrogen atom. C$_m$ denotes the midpoint of the C$_2$−C$_3$ bond. In the case of *syn*-PO−H$_2$O, $\theta_2$ was fixed at the ab initio value during the structural fit. The results are reported in Table 6, together with the corresponding values from the ab initio calculations for comparison. To facilitate comparison with other ether−water complexes, the values for $\angle$(ring-O$_{epoxy}$···H) and $R_{CM}$ were then calculated from the obtained structures of both conformers and are also listed in Table 6. From Table 6, one can see that the intermolecular hydrogen bond angles $\angle$(ring-O$_{epoxy}$···H) and $\phi$ are similar for *anti*-PO−H$_2$O and EO−H$_2$O. This is not surprising because the additional methyl group is on the opposite side of the hydrogen bond in *anti*-PO−H$_2$O. Therefore, the effect of the methyl group is not expected to be dramatic. In contrast, the hydrogen bond angle $\phi$ is much closer to linearity for *syn*-PO−H$_2$O as compared to *anti*-PO−H$_2$O and EO−H$_2$O.

(33) Cook, R. L.; De Lucia, F. C.; Helminger, P. *J. Mol. Spectrosc.* **1974**, *53*, 62−76.

**Table 7.** Comparison of the H-Bonding Force Constants, Stretching Frequencies, and Binding Energies for Several Water Containing Complexes[a]

|  | syn-PO–$H_2O$ | anti-PO–$H_2O$ | EO–$H_2O$[b] | $H_2O$–$H_2O$[c] |
|---|---|---|---|---|
| $k_s$/Nm$^{-1}$ | 8.9 | 5.0 | 7.3 | 10.8 |
| $\nu_s$/cm$^{-1}$ | 105 | 79 | 98 | 143 |
| $\Delta E$/kJ mol$^{-1}$ | 7.2 | 5.0 | 4.9 | 8.0 |
| $v_{harm}$/cm$^{-1}$ | 177 | 177 | 198 | 166 |

[a] The harmonic frequencies were calculated based on the MP2/6-311++G(d,p) geometries and are scaled by a factor of 0.97. [b] Calculated using the experimental results from ref 5. [c] Calculated using the experimental results from ref 36.

## Conformational Stability and Hydrogen Bond Strength

The intermolecular hydrogen bond strength can be measured using the corresponding stretching force constant estimated with a model developed by Read et al.[34] The experimental rotational and centrifugal distortion constants were used in eq 1[34] to calculate the stretching force constant, provided that the stretching coordinate is near-parallel to the *a*-axis. In the cases of the two PO–$H_2O$ conformers, this condition is approximately satisfied because the angle between the *a*-axis and the intermolecular O···H bond is 20.4° and 18.8° for the *syn*- and *anti*-configurations, respectively, based on the ab initio calculations. In eq 1, $\mu$ is the reduced mass of the complex, *B*, *C* and $D_J$ are the spectroscopic constants listed in Tables 4 and 5, and $R_{CM}$ is the separation between the centers-of-mass of the two subunits, listed in Table 6. The related vibrational frequency $\nu_s$ can be calculated using eq 2.[35] The binding energy $\Delta E$ can then be estimated using eq 3, assuming a Lennard–Jones potential function.[35] The results are summarized in Table 7 together with the corresponding values for EO–$H_2O$[5] and $H_2O$–$H_2O$.[36] The harmonic frequencies from the MP2/6-311++G(p,d) calculations, scaled with an empirical factor 0.97, are also included in Table 7 for comparison.

$$k_S = 16\pi^4(\mu R_{CM})^2[(B^2 + C^2)^2 + 2(B^4 + C^4)]/hD_J \quad (1)$$

$$\nu_S = 1/2\pi(k_S/\mu)^{1/2} \quad (2)$$

$$\Delta E = (1/72)k_S R_{CM}^2 \quad (3)$$

The ratio of the values of $k_s$ for *syn*- and *anti*-PO–$H_2O$ is ~1.8 and ~2.0 for *syn*- and *anti*-PO–$D_2O$, indicating that the O···H–O intermolecular hydrogen bond is weaker for the *anti*-configuration than for the *syn*-conformer. This agrees qualitatively with the fact that higher intensities were observed for all isotopomers of *syn*-PO–$H_2O$ than for the corresponding *anti*-PO–$H_2O$ isotopomers.

The order of stability for the three complexes is *syn*-PO–$H_2O$ > *anti*-PO–$H_2O$ ≥ EO–$H_2O$, according to the experimentally estimated binding energies ($\Delta E$s). The relationship between the experimentally observed intensities of different conformers in a molecular beam environment, their relative stabilities, and the interconversion barriers between them were discussed in details by Godfrey et al. for glycolic acid and

histamine.[37] They found that the thermal equilibrium of the conformers prior to jet expansion was preserved if the interconversion barriers were high enough. In the cases of the much less strongly bound rare gas van der Waals clusters, dramatic isotopic enrichments were reported.[38] For example, transitions of $^{22}$Ne$_2$Ar (0.64% abundance) were found to be stronger than those of $^{20}$Ne$^{22}$NeAr (16% abundance). For the systems with such low binding energies, the repeated dissociation and reformation in the molecular expansion process leads to an equilibrium distribution in which the heavier species with lower zero-point energy is greatly enriched at the low temperature achieved in the expansion. We expect the dissociation and recombination effect to be small for the much more strongly bound hydrogen bonded PO–$H_2O$. At the preexpansion temperature of 298 K, an abundance ratio of ~2.4:1 is calculated for *syn*- vs *anti*-PO–$H_2O$ from the experimentally estimated energy difference of 2.2 kJ/mol. At the very low temperature of 1 K in the molecular expansion environment, there would be only a negligible amount of *anti*-PO–$H_2O$ if there were significant collisional relaxation. The detection of both conformers with comparable intensities suggests that the interconversion barrier between these two conformers is high enough to minimize the effect of collisional relaxation. A possible transition state, connecting these two conformers where the water molecule lies in the ring plane, was identified in the ab initio calculation. It is a first-order saddle point with one imaginary frequency of −193 cm$^{-1}$, corresponding to the out of plane wagging motion of the water moiety. The $O_{epoxy}$···H hydrogen bond length was calculated to be 2.252 Å and the raw binding energy for this transition state is −19.88 kJ/mol, at the MP2/6-311++G(d,p) level. The barrier height was estimated to be ~800 cm$^{-1}$. One would therefore expect the abundance ratio at the preexpansion temperature to be approximately preserved in the beam environment. This is roughly consistent with the experimentally observed intensity ratio of about 1.8:1.

We further examine the intensity ratio for the D- and H-bonded isomers in the HOD containing PO–water complex. In the hydrogen bonding molecule-water complexes, the D-bonded species is often substantially enriched in the jet expansion because of its lower zero-point energy and the collisional relaxation through the tunneling motion that interchanges the D and H atoms of water. For example, only the D-bonded isomer was detected in 1,4-dioxane-DOH,[18] and a 3:1 ratio in favor of EO–DOH over EO–HOD,[5] was reported. The differences in zero-point energies between H- and D-bonded species are −0.88 kJ/mol for *syn*-PO-water and −0.86 kJ/mol for *anti*-PO–water, almost the same as for EO–$H_2O$. This means an abundance ratio of ~1.4:1 for the D-bonded species over H-bonded species at the preexpansion temperature of 298 K, for *syn*-PO–water, *anti*-PO–water, and EO–water. The experimental intensity ratio for PO–DOH over PO–HOD is about 1.5:1, indicating that very little collisional relaxation through the hydrogen tunneling motion occurs for PO–water in the jet expansion. The presence of a relatively high barrier is further supported by the fact that no tunneling splitting due to $H_2O$ was detected experimentally for PO–$H_2O$. Additionally,

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(35) Bettens, R. P. A.; Spycher, R. M.; Bauder, A. *Mol. Phys.* **1995**, *86*, 487−511.
(36) Dyke, T. R.; Mack, K. M.; Muenter, J. S. *J. Chem. Phys.* **1977**, *66*, 498−510.

(37) Godfrey, P. D.; Rodgers, F. M.; Brown, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 2232−2239; Godfred, P. D.; Brown, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 10724−10732.
(38) Xu, Y.; Jäger, W. *J. Chem. Phys.* **1997**, *107*, 4788−4796.

the observed intensity ratios suggest that the tunneling barrier is higher for PO−water than that of EO−water.

The above discussions indicate that the intermolecular hydrogen bond in *syn*-PO−$H_2O$ is stronger and the monomer subunits are more rigidly locked in their positions than in EO−$H_2O$. The differences between *anti*-PO−$H_2O$ and EO−$H_2O$, on the other hand, are less prominent. We attribute this observation to the additional stabilizing effect of the methyl group to the hydrogen bond and examine the roles of the weak secondary H-bonds, i.e., the $H_2O\cdots H-C$ noncovalent interactions, in these complexes. In the *syn*-configuration, the intermolecular distance of $H_2O\cdots H-CH_2$ is 2.71 Å, considerably shorter than 3.06 Å for $H_2O\cdots H-CH$. The intermolecular separations of $H_2O\cdots H-C$ and $H_2O\cdots H-CH$ in the anti-configuration are 2.95 and 2.97 Å, respectively. The above observed trend was also supported by the MP2/6-311++G(d,p) calculations. These weak secondary hydrogen bonds can be classified as *improper-blue shifted* H-bonds and were investigated systematically by Hobza and co-workers.[39] One character of this type of H-bond is a decrease in the C−H bond length when the C−H bond gets involved in the hydrogen bond. This is manifested in the *syn*-PO−$H_2O$ species where the bonded and the nonbonded C−H bond lengths in $H_2O\cdots H-CH_2$ are 1.092 Å and 1.094 Å, respectively, from the MP2/6-311++G(d,p) ab initio calculations, in good agreement with the average shortening of 0.002 Å as reported in those studies.[39]

## Conclusions

The PO−water complex was investigated using rotational spectroscopy and ab initio methods for the first time. Two structural conformers, i.e., *syn*-PO−$H_2O$ and *anti*-PO−$H_2O$, were detected experimentally. The conformational stability and the hydrogen bond strength of the PO−$H_2O$ conformers were established using the experimental spectroscopic constants based on a pseudo-diatomic model and were further discussed using the derived structures. The barrier to interconversion between the two distinct structural minima was evaluated with ab initio calculations and discussed in terms of the observed intensities of the two conformers. A stabilizing contribution of the methyl group to the intermolecular hydrogen bond was demonstrated with the experimental observations.

**Supporting Information Available:** Completion of the ref 20. Summary of the detailed calculation results with all three basis sets for the normal and deuterated species. Summary of all the measured transition frequencies of the minor isotopomers. Cartesian coordinates for the two configurations of the PO−$H_2O$ complex obtained with the ab initio calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

(39) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253−4264.

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