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# An ab Initio MO Study on the Structures and Electronic States of Hydrogen-Bonded $O_3$−HF and $SO_2$−HF Complexes

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Ab initio molecular orbital (MO) calculations have been carried out for base−hydrogen fluoride (HF) complexes (base = $O_3$ and $SO_2$) in order to elucidate the structures and energetics of the complexes. The ab initio calculations were performed up to the QCISD(T)/6-311++G(d,p) level of theory. In both complexes, hydrogen-bonded structures where the hydrogen of HF orients toward one of the oxygen atoms of bases were obtained as stable forms. The calculations showed that cis and trans isomers exist in both complexes. All calculations for the $SO_2$−HF complex indicated that the cis form is more stable in energy than the trans form. On the other hand, in $O_3$−HF complexes, the stable structures are changed by the ab initio levels of theory used, and the energies of the cis and trans forms are close to each other. From the most sophisticated calculations (QCISD(T)/6-311++G(d,p)//QCISD/6-311+G(d) level), it was predicted that the complex formation energies for cis $SO_2$−HF, trans $SO_2$−HF, cis $O_3$−HF, and trans $O_3$−HF are 6.1, 5.7, 3.4, and 3.6 kcal/mol, respectively, indicating that the binding energy of HF to $SO_2$ is larger than that of $O_3$. The harmonic vibrational frequencies calculated for cis $O_3$−HF and cis $SO_2$−HF complexes were in good agreement with the experimental values measured by Andrews et al. Also, the calculated rotation constants for cis $SO_2$−HF agreed with the experiment.

## 1. Introduction

$SO_2$ and $O_3$ molecules play an important role in the atmosphere, and these form clusters with negative ions such as $NO_3^-$, $Cl^-$, and others.[1] The clusters exhibit high binding energies and have been extensively studied experimentally.[1] On the other hand, weakly bound complexes of $SO_2$ and $O_3$ with hydrogen halide such as HF and HCl are scarcely studied, although these complexes are also of particular interest in the atmosphere.

Fourier transform infrared (FT-IR) spectra for $SO_2$−HF complexes in solid argon were measured by Andrews et al.[2,3] They observed that the $SO_2$ molecule can form a weakly bound complex with HF in solid argon at 25 K. The stretching mode of the HF molecule (3807 cm$^{-1}$) is red-shifted by forming the $SO_2$−HF complex, meaning that weak interaction between HF and $SO_2$ occur in the formation of the complex. Their FT-IR experiments showed that the structure of $SO_2$−HF is composed of the cis form as a stable structure. The structure of the $SO_2$−HF complex in a pulse nozzle beam was determined by means of FT microwave spectroscopy.[4] The rotational constants were measured to be $A = 16502.772$ MHz, $B = 2100.308$ MHz, and $C = 1853.642$ MHz. From these data, it is indicated that $SO_2$−HF has the cis form in the gas phase.

The FT-IR spectrum of the $O_3$−HF complex in argon matrixes was also measured by Andrews et al.:[2,3] the H−F stretching mode of the HF molecule and three modes of $O_3$ in the $O_3$−HF complex were measured to be 3802.6, 1115.7, 1026.9, and 713.2 cm$^{-1}$, respectively. This feature is very analogous to that of the $SO_2$−HF complex. These results imply that both molecules $SO_2$ and $O_3$ form similar complexes with the HF molecule. From the results of the experiments using isotope oxygen in the $O_3$ molecule, they suggested that one of the $O_3$ molecules interacts weakly with the hydrogen of HF, and both complexes take the cis form in solid argon matrixes.

There are a few reports of ab initio molecular orbital (MO) calculations of the complexes $SO_2$−HF and $O_3$−HF.[5−7] On the basis of the Hartree−Fock (HF)/STO-3G calculations, Friedlander et al. suggested that $SO_2$ forms a complex with HF by a hydrogen bond between H and O atoms, while one of the oxygen atoms of $SO_2$ binds to the hydrogen of HF.[5] The binding energy was calculated to be 5.2 kcal/mol. Carrol et al. calculated the structures of $SO_2$−HF and $O_3$−HF molecules using the HF/6-31G** method.[6,7] They suggested that the complex has two isomers (cis and trans forms) as stable structures. The stabilization energies for $SO_2$−HF(cis), $SO_2$−HF(trans), and $O_3$−HF (cis) were calculated to be 4.7, 4.9, and 3.1 kcal/mol at the HF/6-31G** level.

Although a few ab initio MO calculations were thus carried out by several groups, there is no ab initio calculation with more accurate wave functions and including the electron correlation, which are important in elucidating the interaction between base (proton acceptor) and HF molecule (proton donor). In the present study, the structures and electronic states of the $SO_2$−HF and $O_3$−HF complexes are predicted on the basis of ab initio calculations including electron correlation (MP4SDQ, QCISD, and QCISD(T) methods). The harmonic vibrational frequencies are calculated and compared with the experiments.

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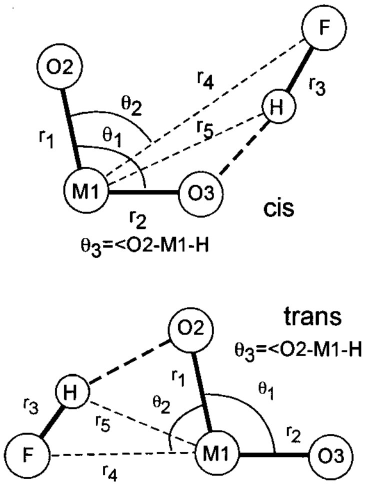

**Figure 1.** Structures and geometrical parameters of base−HF systems.

## 2. Computational Methods

Ab initio MO calculations were carried out using the GAUSSIAN94 program.[8] The complexes calculated in the present work are weakly bound complexes, so that the basis set superposition error (BSSE) would strongly affect the binding energy. Therefore, we chose carefully the basis sets in the binding energy calculations.[9] The geometry optimizations of isolated molecules $SO_2$, $O_3$, HF, and weakly bound complexes ($SO_2$−HF and $O_3$−HF) were carried out at three levels of theory: QCISD/6-31G*, MP4SDQ/6-311+G*, and QCISD/6-311+G*. In addition, the total energies were further calculated at the MP4SDQ/aug-cc-pVDZ and QCISD(T)/6-311++G(d,p) levels using QCISD/6-311+G* optimized geometries in order to obtain relative energies between cis and trans forms of the complexes. The vibrational frequencies of the complexes and isolated molecules were calculated by QCISD/6-31G* method.

## 3. Results

**I. $SO_2$−HF Complex. A. Structures and Energetics of $SO_2$−HF Complexes.** The structure of the $SO_2$−HF complex is fully optimized at several levels of theory. The geometrical parameters are illustrated in Figure 1, while the optimized parameters are given in Table 1. We calculated the structure of the $SO_2$−HF complex at the MP4SDQ and QCISD levels of theory. Both calculations gave similar structures, so the result of only the QCISD calculation is given in Table 1. The geometry optimizations showed that two isomers (i.e., cis and trans forms) were obtained at all levels of theory as global minima. In both forms, the hydrogen of HF orients toward one of the oxygen atoms of $SO_2$. First, we would explain the structure for the cis form. The most sophisticated calculation (QCISD/6-311+G*) showed that the S−O distances of $SO_2$−HF are not equivalent each other ($r_1 = 1.4467$ and $r_2 = 1.4557$ Å), while one of the S−O bonds of $SO_2$ is elongated and the other one is shortened with respect to those of free $SO_2$ ($r_{S-O} = 1.4503$ Å and angle ∠O−S−O is 118.59°). The S−O bond interacting with HF is elongated. The H−F distance of the complex is calculated to be 0.9247 Å ($=r_3$), which is slightly elongated relative to that of the free HF molecule (0.9210 Å). The angle ∠O−S−O of the complex is calculated to be 118.02°, which is slightly narrow compared with that of free $SO_2$. The intermolecular distances between $SO_2$ and HF are 3.2499 Å for the S−H distance ($r_5$) and 4.1621 Å for the S−F distance ($r_4$). The nearest distance (i.e., $O_3$−H distance) is calculated to be 1.9072 Å. In the trans form of $SO_2$−HF, the structure of the $SO_2$ moiety is slightly changed by the complex formation as well as the cis form. The H−F distance is slightly elongated with respect to that of free HF (0.9246 vs 0.9210 Å), and the angle ∠O−S−O is calculated to be 117.66°, which is slightly narrow compared with that of free $SO_2$ (118.59°). The S−O bond formed by the hydrogen bond with the HF molecule is slightly elongated with respect to that of the free $SO_2$ molecule (1.4557 vs 1.4503 Å). These features are very similar to those of the cis form.

**Table 1.** Optimized Parameters[a] for the $SO_2$−HF and $O_3$−HF Complexes Calculated by the QCISD Method

| | $SO_2$−HF | | $O_3$−HF | |
|---|---|---|---|---|
| form | 6-31G* | 6-311+G* | 6-31G* | 6-311+G* |
| cis | | | | |
| r1 | 1.4577 | 1.4467 | 1.2568 | 1.2384 |
| r2 | 1.4676 | 1.4557 | 1.2989 | 1.2751 |
| r3 | 0.9382 | 0.9247 | 0.9366 | 0.9235 |
| $r_4$ | 3.9951 | 4.1621 | 3.584 | 3.7734 |
| $r_5$ | 3.1194 | 3.2499 | 2.7203 | 2.8936 |
| $\theta_1$ | 118.56 | 118.02 | 117.13 | 117.70 |
| $\theta_2$ | 85.94 | 100.92 | 72.16 | 74.20 |
| $\theta_3$ | 90.94 | 98.56 | 76.31 | 79.07 |
| $D^b$ | 0.0 | 0.0 | 0.0 | 0.0 |
| trans | | | | |
| r1 | 1.4688 | 1.4561 | 1.3129 | 1.2848 |
| r2 | 1.4590 | 1.4461 | 1.2494 | 1.2326 |
| r3 | 0.9392 | 0.9246 | 0.9375 | 0.9245 |
| r4 | 3.0969 | 4.0387 | 2.9611 | 3.3865 |
| r5 | 2.7557 | 3.1878 | 2.4333 | 2.6522 |
| $\theta_1$ | 117.73 | 117.66 | 116.67 | 117.49 |
| $\theta_2$ | 62.80 | 27.52 | 70.74 | 56.98 |
| $\theta_3$ | 45.40 | 21.75 | 54.15 | 46.22 |
| $D^b$ | 180.0 | 180.0 | 180.0 | 180.0 |

[a] Bond lengths and angles are in angstroms and in degrees, respectively. [b] Dihedral angle of ∠O−M−O−F: $D = 0.0°$ (cis) and $D = 180°$ (trans).

In order to check for the existence of another local minimum of the complex (i.e., nonplanar and $C_{2v}$ structures), the geometry optimizations are done from several starting points. However, an energy minimum except for the cis and trans forms was not found, meaning that cis $SO_2$−HF and trans $SO_2$−HF are the isomers of the $SO_2$−HF complex.

The total energies of the complexes and relative energies between cis and trans forms are summarized in Table 2. The cis form is more stable in energy than the trans form at all levels of theory, although the difference of the energy is quite small. For example, the QCISD(T)/6-311++G(d,p)//QCISD/6-311+G* calculations shows that the cis form is 0.23 kcal/mol more stable than the trans form. The binding energies are calculated in the range 4.9−6.4 kcal/mol for the cis form. In the trans form, the binding energies are calculated to be 5.0−6.9 kcal/mol, which values are comparable to those of the cis form. However, each level of theory indicated that the cis form is more stable in energy than the trans form.

For comparison with the experiment, the rotational constants of cis and trans $SO_2$−HF complexes (*A*, *B*, and C) are calculated at the QCISD/6-311+G* level. The result is given in Table 3 together with the experimental values measured by Fillery-Travis

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(8) Ab initio MO calculation program: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman; J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(9) BSSE of the 6-311++G** basis set was estimated by about ~0.5 kcal/mol in the present system using the counterpoise method. This value is comparable to that in refs 6 and 7.

**Table 2.** Total Energies (in au) Calculated at Several Levels of Theory[a]

| method | $SO_2$−HF cis | $SO_2$−HF trans | $O_3$−HF cis | $O_3$−HF trans |
|---|---|---|---|---|
| MP4SDQ/aug-cc-pVDZ | −648.03068(0) | −648.03032(0.22) | −325.20008(0) | −325.19966 (0.26) |
| CCSD/aug-cc-pVDZ | −648.02473(0) | −648.02439(0.21) | −325.19686(0) | −325.19654 (0.20) |
| QCISD(T)/aug-cc-pVDZ | −648.05491(0) | −648.05454(0.23) | −325.23756(0) | −325.23735 (0.13) |
| MP4SDQ/6-311++G(d,p) | −648.03068(0) | −648.03032(0.22) | −325.25274(0) | −325.25270 (0.02) |
| QCISD/6-311++G(d,p) | −648.02932(0) | −648.02898(0.21) | −325.24823(0) | −325.24828 (−0.03) |
| QCISD(T)/6-311++G(d,p) | −648.05686(0) | −648.05649(0.23) | −325.29161(0) | −325.29184 (−0.14) |

[a] The structures of the complexes optimized at the QCISD/6-311+G(d,p) level are used in the energy calculations. Relative energies between cis and trans forms (in kcal/mol) are given in parentheses.

**Table 3.** Calculated and Experimental Rotational Constants (in GHz) and Geometrical Parameters for the $SO_2$−HF and $O_3$−HF Complexes

| | rotational constant *A* | rotational constant *B* | rotational constant *C* | *R*(O−F)[a,b] | ∠S−O−F[b] |
|---|---|---|---|---|---|
| calcd | | | | | |
| cis $SO_2$−HF | 17.6747 | 1.9840 | 1.7838 | 2.8314 | 150.7 |
| trans $SO_2$−HF | 55.4760 | 1.7302 | 1.6778 | 2.8287 | 218.1 |
| cis $O_3$−HF | 15.1960 | 3.0860 | 2.5651 | | |
| trans $O_3$−HF | 38.3233 | 2.4484 | 2.3014 | | |
| exptl[c] | | | | | |
| $SO_2$−HF | 16.502775 | 2.100308 | 1.853642 | 2.818 | 144.94 |

[a] Nearest O−F distance in the $SO_2$−HF complex. [b] Bond lengths and angles are in angstroms and in degrees, respectively. [c] Experimental values are cited from ref 4.

**Table 4.** Harmonic Vibrational Frequencies for the Cis and Trans $SO_2$−HF Complex (in cm$^{-1}$)[a]

| mode | cis | trans | free $SO_2$ | shift cis | shift trans |
|---|---|---|---|---|---|
| 1 | 3971.3 (458.1) | 3963.0 (174.0) | | | |
| 2 | 1345.9 (117.9) | 1339.8 (158.3) | 1220.7 | +125.2 | +119.1 |
| 3 | 1151.5 (43.3) | 1145.3 (28.9) | 918.8 | +232.7 | +226.5 |
| 4 | 538.7 (72.7) | 541.8 (320.6) | 717.3 | −178.6 | −175.5 |
| 5 | 474.0 (172.6) | 523.7 (137.6) | | | |
| 6 | 450.4 (110.1) | 444.7 (162.8) | | | |
| 7 | 161.7 (1.6) | 174.3 (5.8) | | | |
| 8 | 128.9 (2.9) | 97.6 (14.6) | | | |
| 9 | 41.6 (0) | 85.0 (15.5) | | | |

[a] The calculations were carried out at the QCISD/6-31G* level. Infrared intensities are given in parentheses (in km/mol). The frequency shifts caused by the complex formation are also given. The frequency of the H−F stretching mode of HF and its IR intensity are calculated to be 4017 cm$^{-1}$ and 75 km/mol, respectively.

and Legon.[4] As clearly seen in Table 3, all rotational constants calculated for cis $SO_2$−HF are in good agreement with the experiment. On the other hand, the rotational constants for the trans form are much different from those of the experiment: in particular, the calculated rotational constant *A* is significantly larger than the experimental value (55.4760 vs 16.502775 GHz). The calculated and experimental intermolecular distances and angles of $SO_2$−HF complexes are also given in Table 3. As well as the rotational constants, the structural parameters calculated for the cis form agree excellently with the experiment,[4] whereas those of the trans form disagree.

**B. Harmonic Vibrational Frequencies.** The vibrational frequencies of free $SO_2$ and the cis and trans forms of $SO_2$−HF are calculated at the QCISD/6-31G* level. The results are listed in Table 4. First, we explain the results of the cis form. The highest frequency (mode 1) corresponds to the H−F stretching mode of the complex, which is slightly red-shifted from that of the free HF molecule (3971 vs 4017 cm$^{-1}$). Three modes of free $SO_2$ in vacuo are calculated to be $\nu_3 = 1221$ cm$^{-1}$, $\nu_1 = 919$ cm$^{-1}$, and $\nu_2 = 713$ cm$^{-1}$. These modes are shifted to $\nu_3 = 1346$ cm$^{-1}$, $\nu_1 = 1152$ cm$^{-1}$, and $\nu_2 = 539$ cm$^{-1}$ by forming the complex with HF. The magnitude of the shift is calculated to be $\Delta\nu_3 = +125$ cm$^{-1}$, $\Delta\nu_1 = +233$ cm$^{-1}$, and $\Delta\nu_2 = -179$ cm$^{-1}$, suggesting that all modes of $SO_2$ are largely shifted by the complex formation. The feature of the frequency shifts is consistent with the experimental values ($\Delta\nu_3 = +49$ cm$^{-1}$, $\Delta\nu_1 = +330$ cm$^{-1}$, and $\Delta\nu_2 = +11$ cm$^{-1}$).

For the trans form of $SO_2$−HF, the harmonic vibrational frequencies for three modes of $SO_2$ moiety are calculated to be $\nu_3 = 1340$ cm$^{-1}$, $\nu_1 = 1145$ cm$^{-1}$, and $\nu_2 = 542$ cm$^{-1}$, indicating that the magnitude of the frequency shift is comparable to that of the cis form. The zero point vibrational energies (ZPEs) of the cis and trans forms are calculated to be 11.8 and 12.0 kcal/mol.

**C. Structure of the $SO_2$−HF Complex at 100 K.** As mentioned above, the interaction between HF and $SO_2$ is quite weak. This implies that the structure of the complex is significantly fluxional at finite temperature. In order to elucidate this feature in more detail, we calculated first the structure of $SO_2$−HF at finite temperatures by means of the full dimensional ab initio molecular dynamics method.[10−16] We have chosen three temperatures (10, 50, and 100 K) as simulation temperatures. The calculations showed that the intermolecular distance between HF and $SO_2$ ($=r_4$) vibrates in the range 4.051−4.312 Å (the amplitude is 0.261 Å). Thus, the present dynamics calculations indicate that the complex is very floppy and flexible for the intermolecular motion. Also, it is indicated that thermal conversion between cis and trans forms does not take place in the temperature range 10−100 K.

**II. $O_3$−HF Complex. A. Structures and Energetics of $O_3$−HF Complexes.** The optimized geometrical parameters of the $O_3$−HF complex are given in Table 1. The geometry optimization showed that two isomers (cis and trans forms) were obtained as stable forms as well as $SO_2$−HF. In both forms, the hydrogen of HF orients toward one of the terminal oxygen atoms of $O_3$,

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(16) Program code of the direct ab initio dynamics calculation was created by our group.

**Table 5.** Harmonic Vibrational Frequencies for the Cis and Trans $O_3$−HF Complex (in $cm^{-1}$)

| mode | cis | trans | free $O_3$ | shift cis | shift trans | shift exptl |
|---|---|---|---|---|---|---|
| 1 | 3990.3 (306.4) | 3972.9 (305.1) | | | | |
| 2 | 1278.8 (39.0) | 1325.3 (39.4) | 1220.7 | +58.1 | +104.7 | +12.0 |
| 3 | 807.6 (281.7) | 759.7 (78.7) | 918.8 | −111.2 | −159.1 | −12.6 |
| 4 | 710.1 (91.7) | 660.1 (49.6) | 717.3 | −7.2 | −57.2 | +9.6 |
| 5 | 513.4 (156.0) | 475.8 (501.5) | | | | |
| 6 | 413.2 (75.7) | 403.6 (154.1) | | | | |
| 7 | 147.6 (3.1) | 179.5 (8.0) | | | | |
| 8 | 133.5 (1.7) | 87.8 (7.6) | | | | |
| 9 | 55.6 (1.8) | 52.8 (11.3) | | | | |

[a] The calculations were carried out at the QCISD/6-31G* level. Infrared intensities are given in parentheses (in km/mol). The frequency shifts caused by the complex formation are also given.

meaning that the oxygen atoms in the terminal positions of $O_3$ are asymmetric in the complex. All levels of calculations gave similar structures of the complexes, so we would explain the structures of the complexes using the results of the most sophisticated calculations (QCISD/6-311+G*). For the cis form of $O_3$−HF, the O−O distance of the oxygen interacting with the hydrogen ($r_2$) is slightly longer than the other one (1.2751 vs 1.2384 Å). This feature is also obtained for trans form (1.2848 vs 1.2326 Å). The distances of the hydrogen bond in the cis and trans forms are 2.0578 and 2.0106 Å as the O−H distance, respectively. The H−F bond distance becomes longer in the complex formation. These features are similar to those of the $SO_2$−HF complex.

Total energies of the $O_3$−HF complex are given in Table 2 together with the relative energies between cis and trans forms. The cis form is more stable in energy than the trans form when the aug-cc-pVDZ basis set is used in the calculation. On the other hand, the energies of the cis form are almost equivalent or slightly higher in energy than that of trans form in the calculation with the 6-311++G(d,p) basis set. The binding energy for the cis and trans forms of the $O_3$−HF complex are calculated to be 3.4 and 3.6 kcal/mol at the QCISD(T)/6-311++G(d,p) level, respectively. This implies that it is quite difficult to determine the stable form from only the energetics.

The rotational constants of $O_3$−HF are given in Table 3. As well as in $SO_2$−HF, the rotational constant $A$ for the trans form is significantly larger than that of the cis form (55.476 vs 17.675 GHz). This means that the cis and trans forms of $O_3$−HF are easily distinguishable using Fourier transform microwave spectroscopy.

**B. Harmonic Vibrational Frequencies.** The harmonic vibrational frequencies, calculated at the QCISD/6-31G* level of theory, are given in Table 5. The highest frequencies for the cis and trans forms (3990 and 3973 $cm^{-1}$) correspond to the H−F stretching mode of the HF moiety of the complex. These modes are red-shifted by 27 $cm^{-1}$ (cis) and by 44 $cm^{-1}$ (trans) from that of the free HF molecule (4017 $cm^{-1}$). The intensity of the IR spectrum of free HF is largely increased in the complex formation (from 75 to 306 km/mol). The frequencies of the $O_3$ moiety of the complexes and its shifts from those of free $O_3$ are also given in Table 5. The frequency shifts for the cis form are calculated to be +58, −111, and −7 $cm^{-1}$, which are qualitatively comparable to the experimental data (+12, −13, and +10 $cm^{-1}$). On the other hand, the magnitudes of the frequency shifts in the trans form (+105, −159, and −57 $cm^{-1}$) are significantly larger than the experimentally determined values. The ZPEs for the cis and trans forms are 11.5 and 11.3 kcal/mol, respectively. The complex formation energies for the cis and trans forms after the correction of ZPEs are 1.7 and 2.1 kcal/mol, respectively.

## 4. Discussion

**A. Structures of Base−HF Complexes.** From the present calculations, it is predicted that the hydrogen atom of HF orients toward one of the oxygen atoms of bases ($SO_2$ and $O_3$) in both complexes. The oxygen atoms in the terminal positions of the bases are not equivalent: namely, the S−O and O−O bonds interacting with HF are slightly elongated, although its magnitude is significantly small. The bonding between base and HF is composed of a hydrogen bond in which the hydrogen of the HF molecule is bound linearly to the oxygen atom.

Also, the present calculations indicated that HF is bound more strongly to $SO_2$ than $O_3$. The most sophisticated calculations (QCISD(T)/6-311++G(d,p)//QCISD/6-311+G*) showed that the binding energies are 6.05 (cis $SO_2$−HF), 5.74 (trans $SO_2$−HF), 3.41(cis $O_3$−HF), and 3.61 kcal/mol (trans $O_3$−HF). This difference is caused by the difference of the proton affinities in $SO_2$ and $O_3$, as expected by Andrews et al.[2] Actually, the proton affinities of $SO_2$ and $O_3$ are 160.7 and 149.5 kcal/mol, respectively.[17,18]

**B. Comparison with the Experiments. $SO_2$−HF Complex.** The present calculations imply that two isomers (cis and trans structures) are possible as stable structures in both complexes. In the $SO_2$−HF complex, the cis form is more stable in energy than the trans form. Filley-Travis and Legon observed the ground state rotational spectra of $SO_2$−HF by means of a Fourier transform microwave spectrometer.[4] Rotational constants of the complex were measured to be $A = 16.502$ GHz, $B = 2.100308$ GHz, and $C = 1.853642$ GHz. As clearly seen in Table 3, the calculated rotational constants for the cis form are in good agreement with the experiment, whereas those of the trans form disagree. The nearest F−O distances and angle ∠S−O−F for the cis form are in excellent agreement with the experiment. Hence, it is concluded that the most stable structure of $SO_2$−HF in the gas phase is the cis form. The present calculations also indicated that the cis form is stable in energy in low-temperature matrixes because the harmonic vibrational frequencies calculated for the cis form are in good agreement with the experiment by Andrews et al.[2] It should be noted, however, that the calculated frequencies for the trans form are in qualitative agreement with their experiment.

**$O_3$−HF Complex.** The present ab initio MO calculations indicated that both the cis and trans forms exist as stable structures of the $O_3$−HF complex in vacuo. Unfortunately, there is no rotational spectrum of $O_3$−HF as far as we know. Hence, we could not compare directly the calculated structure with experiment. This may be due to the fact that the complex stabilization energy is quite small as predicted by the present calculations. The calculations up to QCISD(T)/6-311++G(d,p)//QCISD/6−31*G* levels of theory did not clearly determine the dominant structure of $O_3$−HF (cis or trans form). However, from a comparison of the theoretical vibrational frequencies with the experiment, it can be suggested that $O_3$−HF exists preferentially as the cis form in matrixes.

In order to consider the contribution of medium effect on the stability in the condensed phase, we calculated dipole moments of two forms. The dipole moments were calculated to be 3.40 D for the cis form and 2.58 D for the trans form, meaning that the cis form is more strongly stabilized by

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(17) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data*. **1998**, *27*, 413.

(18) Proton affinities of $SO_2$ and $O_3$ were calculated to be 158.7 and 147.5 kcal/mol at the QCISD/6-311+G* level, respectively.

dielectric medium effects than the trans form, although the magnitude is small in argon matrixes. Next, we considered the effect of the molecular volume of the complexes. The molecular volume of the cis form is about 15% smaller than that of the trans form. This effect may contribute to the stability of the complex in the condensed phase.

From the present calculations, it can be predicted that rotational constants of cis and trans $O_3$−HF complexes are $A = 15.196$ GHz, $B = 3.086$ GHz, and $C = 2.565$ GHz and $A = 38.323$ GHz, $B = 2.448$ GHz, and $C = 2.301$ GHz, respectively. The rotational constant $A$ of the trans form is about 2.5 times larger than that of the cis form. This feature is the same as that of the $SO_2$−HF complex.

**C. Comparison with Previous Theoretical Studies.** In 1983, Friedlander et al. calculated the structure and complex formation energies for $SO_2$−HF at the ab initio HF/STO-3G level of theory.[5] They found the most stable structure where HF binds linearly to the S−O bond with a separation of 1.8 Å. The HF is bound to the oxygen atom by a hydrogen bond. This feature is essentially similar to that of the present study, although the stable structure is slightly modified by the present study: namely, the cis form is the most stable structure of $SO_2$−HF.

Also, Carrol et al. carried out similar ab initio calculations for the $SO_2$−HF complexes, but a more flexible basis set (6-31G**) was used in the geometry optimization.[6,7] They found two isomers (cis and trans forms) on the ground state surface. The calculations indicated that the cis form is slightly more stable in energy than the trans form at the HF/6-311++G**//HF/6-31G** level, which is in good agreement with the present conclusion.

## 5. Concluding Remarks

In the present calculations, we used the QCISD method with the 6-311+G(d) basis set to obtain the structure of the complexes, and the binding energy and electronic states were further calculated at the QCISD(T)/6-311++G(d,p) level. Using this method, the most stable structure of the $SO_2$−HF complex was explicitly determined. The calculated vibrational frequencies and rotational constants are in good agreement with the experiments. However, the dominant structure of $O_3$−HF was not clearly determined: the total energies of the cis and trans forms are calculated to be quite similar to each other. At this time, we could not solve the question of whether this feature is true or not. More accurate wave functions (for example, multireference (MR) configuration interaction (CI) method with larger basis sets) would be required in order to obtain the relative energies. Despite the several assumptions introduced here, the results enable us to obtain valuable information on the structures and electronic states of the $SO_2$−HF and $O_3$−HF complexes.

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