Infrared absorption of CH3OSO and CD3OSO radicals produced upon photolysis of CH3OS(O)Cl and CD3OS(O)Cl in p-H2 matrices
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Infrared absorption of CH$_3$OS and CD$_3$OS radicals produced upon photolysis of CH$_3$OS(O)Cl and CD$_3$OS(O)Cl in p-H$_2$ matrices

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I. INTRODUCTION

The oxidation of reduced sulfur compounds such as dimethyl sulfide (DMS, CH$_3$SCH$_3$), dimethyl disulfide (DMDS, CH$_3$SSCH$_3$), and methanethiol (or methyl mercaptan, CH$_3$SH), plays an important role in the formation of acid rain and cloud in the atmosphere. Hydroxy sulfone (HOSO), plays an important role in the combustion of sulfur-rich fossil fuels. Although theoretical computations predict that CH$_3$OSO is also play an important role in the combustion of fuels containing sulfur species at high temperature, similar to the key action bands of gaseous CH$_3$OSO, produced upon irradiation at 239 nm, might escape from the original cage to yield isolated CH$_3$OSO radicals. © 2012 American Institute of Physics.

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I. INTRODUCTION

The oxidation of reduced sulfur compounds such as dimethyl sulfide (DMS, CH$_3$SCH$_3$), dimethyl disulfide (DMDS, CH$_3$SSCH$_3$), and methanethiol (or methyl mercaptan, CH$_3$SH), plays an important role in the formation of acid rain and cloud in the atmosphere. Hydroxy sulfone (HOSO), plays an important role in the combustion of sulfur-rich fossil fuels. Although theoretical computations predict that CH$_3$OSO is also play an important role in the combustion of fuels containing sulfur species at high temperature, similar to the key action bands of gaseous CH$_3$OSO, produced upon irradiation at 239 nm, might escape from the original cage to yield isolated CH$_3$OSO radicals. © 2012 American Institute of Physics.

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was assigned to the C–O stretching ($v_{10}$) mode. Two weak bands at 2991 ± 6 and 2956 ± 3 cm$^{-1}$ were assigned to the CH$_3$ antisymmetric stretching ($v_2$) and symmetric stretching ($v_3$) modes, respectively, but the important O–S stretching mode was unobserved because of the limited spectral range of the photovoltaic detector.

The matrix-isolation technique is suitable for further spectral investigation of CH$_3$OSO because the sample can be accumulated over an extended period to increase its absorbance so that weaker lines might be observed. Furthermore, because of the small widths of lines and the absence of rotation in matrices because of the low temperature, overlapped bands such as $v_8$ and $v_9$ in gaseous syn-CH$_3$OSO might be resolved in the matrix. The small amount of samples required for matrix-isolation spectroscopy also makes isotopic experiments feasible. For conventional inert-gas matrices, however, the matrix cage effects typically prevent formation of free radicals from the photolysis of chloro compounds in situ because the Cl atom cannot escape from the original cage. The diminished cage effect of the quantum solid p-H$_2$ as a matrix host has been demonstrated to allow the production of free radicals via photofragmentation or bimolecular reactions upon UV irradiation. For example, in our laboratory, irradiation with a mercury lamp at 254 nm of a p-H$_2$ matrix containing CH$_3$I and SO$_2$ at 3.2 K followed by annealing of the matrix produced prominent features at 633.8, 917.5, 1071.1, 1272.5, and 1416.0 cm$^{-1}$ that are attributable to $v_{11}$ (C–S stretching), $v_{10}$ (CH$_3$ wagging), $v_4$ (SO$_2$ symmetric stretching), $v_7$ (SO$_2$ antisymmetric stretching), and $v_6$ (CH$_3$ scissoring) modes of CH$_3$SO$_2$, respectively. These results demonstrate that the cage effect of solid p-H$_2$ is diminished so that CH$_3$ radicals, produced via UV photodissociation of CH$_3$I in situ, might react with SO$_2$ to form CH$_3$SO$_2$ during irradiation and upon annealing. The present work on CH$_3$SO$_2$ isolated in a p-H$_2$ matrix extends the previous observation of two transient IR absorption bands of gaseous CH$_3$SO$_2$ at 1280 and 1076 cm$^{-1}$ (Ref. 30) to five lines to include the important one associated with the C–S stretching mode. We have extended the project to matrix-isolated CH$_3$OSO and CD$_2$OSO produced via UV photolysis of a p-H$_2$ matrix containing CH$_3$OS(O)Cl and CD$_2$OS(O)Cl, respectively. Eleven fundamental vibrational modes of syn-CH$_3$OSO, including the C–O, O–S, and S=O stretching modes are characterized.

II. EXPERIMENTS AND COMPUTATIONS

The matrix sample substrate is a gold-plated copper block, cooled to 3.2 K with a closed-cycle refrigerator system (Janis RDK-415); it also serves as a mirror to reflect the incident IR beam to the detector. Typically, a gaseous mixture of CH$_3$OS(O)Cl/p-H$_2$ (1/300–1/2000, flow rate 14.7–16.1 mmol h$^{-1}$) was deposited over a period of 2–6.5 h. The IR absorption spectra were recorded with a FTIR spectrometer (BOMEM, DA8) equipped with a KBr beam splitter and a HgCdTe detector at 77 K to cover the spectral range 450–4100 cm$^{-1}$. The IR spectrum of the sample at 3.2 K was recorded generally at resolution 0.25 cm$^{-1}$ and averaged with 600 interferometric scans after each stage of the experiment. The IR beam was passed through a filter (2.40ILP-50, Andover Corp.) to block light with wavenumber greater than 4100 cm$^{-1}$ to avoid reaction of Cl with vibrationally excited H$_2$ produced after absorption of the IR light.

A medium-pressure mercury (Hg) lamp (200 W, China Electric, Model H200X) coupled with an interference filter passing either 239 ± 20 nm or 254 ± 10 nm serves as a source for initial photolysis. Transmission for Hg emission lines near 253.7 and 226.2 nm is ∼6.5% and 10.5%, respectively, for the 239 nm filter and ∼15% and 0%, respectively, for the 254 nm filter.

Normal H$_2$ (99.9999%, Scott Specialty Gases), after passing through a trap at 77 K, entered a copper cell filled with hydrous iron(III) oxide catalyst (Aldrich) and cooled with a closed-cycle refrigerator (Advanced Research Systems, DER04AF) for p-H$_2$ conversion. The efficiency of conversion was controlled by the temperature of the catalyst; the conversion temperature is typically set at 13 K at which the concentration of o-H$_2$ is less than 40 ppm.

CH$_3$OS(O)Cl was synthesized on slow addition of CH$_3$OH (∼1 g) to equal moles of Cl$_2$SO under stirring, followed by further addition of CH$_3$OH (0.4 g) and stirring for 30 min until no bubble was observed. The products were stored in a refrigerator at 253 K for a few days for completion of the reaction before being pumped under vacuum at 193 K to remove HCl and SO$_2$. For the synthesis of CD$_3$OS(O)Cl, CH$_3$OH was replaced with CD$_3$OH. CH$_3$OH (Absolute Grade, 100.0%, J. T. Baker), CD$_3$OH (isotopic purity 99.5%, Cambridge Isotope Laboratories), and Cl$_2$SO (>98%, Riedel-de Haën) were used without further purification.

The geometry and vibrational wavenumbers of CH$_3$OSO are well characterized. In this work, we employed the GAUSSIAN 09 program to calculate the harmonic and anharmonic vibrational wavenumbers, and IR intensities of CH$_3$OSO and CD$_3$OSO with the B3P86 density-functional theory. Dunning’s correlation-consistent polarized-valence triple-zeta basis set, augmented with s, p, d, and f functions (aug-cc-pVTZ), was employed. Harmonic vibrational wavenumbers were calculated analytically at each stationary point. The anharmonic effects were calculated with a second-order perturbation approach using effective finite-difference evaluation of the third and semidiagonal fourth derivatives.

III. EXPERIMENTAL RESULTS

A. Photolysis of CH$_3$OS(O)Cl/p-H$_2$ matrices

The IR spectrum of a sample of CH$_3$OS(O)Cl/p-H$_2$ (1/500) at 3.2 K is shown in Fig. 1(a) for some selected spectral regions. Lines at 3043.1, 3020.8, 2987.4, 2978.1, 2962.9, 1464.2, 1453.4, 1426.4, 1234.8, 1223.1, 1166.0, 965.2, 733.7, and 560.1 cm$^{-1}$ are due to CH$_3$OS(O)Cl; those shown in Fig. 1(a) are marked as *. Our experimental observations are consistent with the anharmonic vibrational wavenumbers predicted for syn-CH$_3$OS(O)Cl, with four intense IR bands at 1231, 970, 709, and 453 cm$^{-1}$ and some weaker
We found that irradiation of the matrix sample with the medium-pressure Hg lamp produced more intense lines of the CH$_3$OSO product in the initial stage of photolysis when a 239 ± 20 nm filter was used than when a 254 ± 10 nm filter was used, presumably CH$_3$OSO was dissociated with the UV light near 254 nm more readily than near 226 nm. We describe here only experiments with a filter passing light in the region 239 ± 20 nm.

Among various experiments, the following procedure provided the best results for identification of the CH$_3$OSO product: (1) irradiation of the matrix with light near 239 ± 20 nm for 1.5 h, and (2) further irradiation for additional 1.5 h. The matrix was maintained at 3.2 K during the photolysis and the recording of spectra.

Upon irradiation of the CH$_3$OS(O)Cl/p-H$_2$ (1/500) matrix at 239 ± 20 nm for 1.5 h, lines due to CH$_3$OS(O)Cl (marked * in Fig. 1(a)) and SO$_2$ decreased in intensity, as shown in Fig. 1(b); those of (CH$_3$O)$_2$SO (marked # in Fig. 1(a)), and Cl$_2$SO also decreased slightly. Trace (b) is a difference spectrum recorded upon irradiation near 239 ± 20 nm for 1.5 h after deposition. The difference spectrum was obtained on subtracting the spectrum recorded in the preceding step from that recorded after this step; features pointing upward thus indicate production, whereas those pointing downward indicate destruction. Trace (c) is a difference spectrum obtained after irradiation near 239 ± 20 nm for an additional 1.5 h. Some features increased in intensity more in this step, whereas some increased less. To differentiate this behavior, we subtracted trace (b) from trace (c), as shown in trace (d). The features pointing upwards in traces (b) and (c) but downwards in trace (d) are associated with species that were produced more in the initial stage and less in the second stage; they are indicated as group A. The features pointing upward in traces (b), (c), and (d) are thus associated with species that were produced more in the second stage than in the first stage; they are indicated as group B.

Lines in group A at 3028.4, 2999.5, 2950.4, 1452.0, 1417.8, 1165.2, 1152.1, 1147.8, 989.7, and 714.5 cm$^{-1}$ show similar relative intensities in separate stages of various experiments; the line at 1147.8 cm$^{-1}$ is overlapped with another one at 1147.4 cm$^{-1}$. These lines are assigned to syn-CH$_3$OSO, to be discussed in Sec. IV A. Lines in group B at 3651.9, 3038.5, 1457.6, 1332.1, 1179.2, and 1047.0 cm$^{-1}$ have small intensities except the one at 1179.2 cm$^{-1}$. These features are readily assigned to CH$_2$OH because they have vibrational wavenumbers similar to those reported for CH$_2$OH in Ar matrices at 3650, 1459, 1334, 1138, and 1048 cm$^{-1}$, with the latter two being more intense than others. We also observed a line at 943.8 cm$^{-1}$ due to atomic Cl (Ref. 42) and a line of SO at 1136.2 cm$^{-1}$. After prolonged irradiation, weak lines of CH$_3$, CH$_3$SO$_2$, CH$_4$, ClSO$_2$, and Cl$_2$O appeared. CH$_3$ absorbed at 3170.6, 1402.7/1420.3/1401.7, and 624.0 cm$^{-1}$, consistent with the reports for CH$_3$ of absorption at 3171.6/3171.4 ($\nu_1$), 1402.7/1420.4/1401.7 ($\nu_3$), and 624.0 ($\nu_2$). CH$_3$SO$_2$ absorbs at 1273.6/1273.0/1272.5 cm$^{-1}$, similar to the values reported for CH$_3$SO$_2$ produced from the reaction of CH$_3$ + SO$_2$ in a p-H$_2$ matrix. Lines of CH$_3$ were observed at 3025.9/3025.1 ($\nu_3$) and 1308.3 ($\nu_4$), and lines

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) Partial IR spectra of a CH$_3$OS(O)Cl/p-H$_2$ (1/500) matrix after deposition for 3 h (trace a). Lines of CH$_3$OS(O)Cl are marked as * and those of CH$_3$OS(O)Cl impurity are marked as #. (b) Difference spectra of the matrix in (a) after irradiation at 3.2 K and 239 ± 20 nm for 1.5 h. (c) Difference spectra obtained on further irradiation at 3.2 K and 239 ± 20 nm for an additional 1.5 h. (d) Difference spectra obtained on subtracting trace (b) from trace (c). Lines in groups A and B are assigned to syn-CH$_3$OSO and CH$_2$OH, respectively.}
\end{figure}
at 1299.6/1298.7 and 1104.1/1103.1 cm$^{-1}$ might be due to CISO$_2$, consistent with the values 1311.0/1309.6 and 1099.8/1098.2 cm$^{-1}$ reported for CISO$_2$ in an Ar matrix. CISO was also observed at 1169.6 cm$^{-1}$, consistent with 1162.9 cm$^{-1}$ reported in the gaseous phase.

### B. Photolysis of a CD$_3$OS(O)Cl/p-H$_2$ matrix

The IR spectrum of a sample of CD$_3$OS(O)Cl/p-H$_2$ (1/500) at 3.2 K is shown in Fig. 2(a). Lines at 2287.4, 2269.6, 2241.0, 2236.6, 2182.1, 2135.7, 2114.6, 2088.8, 1235.9, 1167.0, 1080.4, 1066.4, 1055.6, 971.8, 924.4, 892.7, 705.6, and 541.3 cm$^{-1}$, as marked * in Fig. 2(a), are due to CD$_3$OS(O)Cl, consistent with the anharmonic vibrational wavenumbers 2280, 2263, 2100, 1234, 1074, 1073, 1044, 967, 919, 887, 688, 530, and 451 cm$^{-1}$ predicted with the B3P86/aug-cc-pVTZ method. Lines at 2280.6, 2277.3, 2258.5, 2207.7, 2202.5, 2187.0, 2183.9, 2156.3, 2140.1, 2117.9, 2092.6, 2085.5, 2081.9, 1215.1, 1159.9, 1099.5, 1096.3, 1085.2, 1082.0, 1070.1, 999.6, 992.3, 963.9, 940.0, 935.5, 721.4, 675.1, 669.8, and 559.9 cm$^{-1}$, as marked # in Fig. 2(a), are due to impurity (CD$_3$O)$_2$SO, consistent with the harmonic vibrational wavenumbers at 2349, 2337, 2329, 2304, 2188, 2174, 1247, 1120, 1103, 1081, 1080, 1069, 1065, 1031, 992, 947, 934, 908, 903, 700, 661, and 547 cm$^{-1}$ predicted with the B3P86/aug-cc-pVTZ method. Line at 983.5 cm$^{-1}$ is due to CD$_3$OH, consistent with value 988 cm$^{-1}$ reported in the gas phase. Lines at 1355.8/1355.4 and 1149.7/1148.7 cm$^{-1}$ are due to SO$_2$ impurity. Lines at 1246.2 and 497.5 cm$^{-1}$ are due to Cl$_2$SO.

Trace (b) of Fig. 2 shows the difference spectrum of the CD$_3$OS(O)Cl/p-H$_2$ (1/500) matrix after irradiation at 239 ± 20 nm for 1 h. Lines due to CD$_3$OS(O)Cl and SO$_2$ decreased in intensity, and lines in two groups; those due to (CD$_3$O)$_2$SO also decreased slightly. Lines in group A that were assigned to syn-CH$_3$OSO in the CH$_3$OS(O)Cl/p-H$_2$ experiments shifted to 2275.9, 2251.9, 2083.3, 1159.7, 1085.5, 1070.3, 1056.0, 976.9, 920.1, 889.0, and 688.9 cm$^{-1}$, as marked A in Fig. 2(a). Those in group B that were assigned to Cl$_2$OH in the CH$_3$OS(O)Cl/p-H$_2$ shifted to 3653.6, 2165.9, 1280.5, 1212.9, 1017.1, and 840.7 cm$^{-1}$.

The $v_2$ band of CH$_3$ observed at 624.0 cm$^{-1}$ in Fig. 1(b) also shifted to 451.8 cm$^{-1}$ for CD$_3$, similar to values 453 and 463 cm$^{-1}$ observed in solid Ar and Ne, respectively.

### IV. DISCUSSION

Gaseous CH$_3$OS(O)Cl at 300 K has an absorption cross section $\sim 8 \times 10^{-19}$ cm$^2$ molecule$^{-1}$ near 248 nm. The possible products after photolysis of CH$_3$OS(O)Cl at 239 ± 20 nm are expected to be CH$_3$OSO + Cl, CH$_3$ + ClSO$_2$, and CH$_3$ + CISO$_2$. According to Alligood et al., only the S=Cl fission channel to produce Cl atom and CH$_3$OSO radical was observed upon photolysis of CH$_3$OS(O)Cl at 248 nm. Some vibrationally excited CH$_3$OSO radicals undergo subsequent dissociation to CH$_3$ + SO$_2$. The dissociation threshold to form CH$_3$OSO + Cl is calculated to be 239 kJ mol$^{-1}$, corresponding to a wavelength of 501 nm. With a filter to pass either 239 ± 20 nm or 254 ± 10 nm, we employed emission from a Hg lamp with the expectation that the light dissociates CH$_3$OS(O)Cl and that the major products are CH$_3$OSO and Cl.

The photolysis of impurities (CH$_3$O)$_2$SO and SO$_2$ must also be considered. The photolysis of (CH$_3$O)$_2$SO at 248 nm was investigated by Alligood et al., who reported the main photodissociation products to be CH$_3$ and CH$_3$OS(O)O. Although SO$_2$ has an absorption cross section $\sim 2 \times 10^{-19}$ cm$^2$ molecule$^{-1}$ at 254 nm (Ref. 50) and $\sim 3 \times 10^{-19}$ cm$^2$ molecule$^{-1}$ at 226 nm, its dissociation threshold of 543 kJ mol$^{-1}$ to form SO + O corresponds to a wavelength of $\sim 220$ nm.

### A. Assignments of lines in group A in the CH$_3$OS(O)Cl/p-H$_2$ experiments to syn-CH$_3$OSO

Considering that CH$_3$OSO is the expected product of photolysis and that the vibrational wavenumbers of five observed lines in group A near 2999.5, 2950.4, 1152.1, 1147.8, and 989.7 cm$^{-1}$ are similar to the values of 2991 ± 6, 2956 ± 3, 1154 ± 3, 1151 ± 3, and 994 ± 6 cm$^{-1}$ reported for gaseous syn-CH$_3$OSO, we contend that lines in group A are likely due to syn-CH$_3$OSO.

As listed in Table I, quantum-chemical calculations using the B3P86/aug-cc-pVTZ method predict that the IR lines of syn-CH$_3$OSO with intensity greater than 10 km mol$^{-1}$ have anharmonic vibrational wavenumbers near 2998.5, 2996 (v$_2$), 1473 (v$_4$), 1448 (v$_5$), 1157 (v$_7$), 1149 (v$_9$), 1144 (v$_9$), 995 (v$_{10}$), and 698 (v$_{11}$) cm$^{-1}$; some of these values are slightly modified from the previous report. Our observed lines in group A at 3028.4, 2995.5, 2950.4, 1465.2, 1452.0, 1417.8, 1165.2, 1152.1, 1147.8, 989.7, and 714.5 cm$^{-1}$ are within 2.3% of the predicted values. The relative IR intensities observed in these experiments are also consistent with the theoretical predictions except those associated with the $v_7$–$v_9$ modes, as compared in Table I. The deviations
IR intensities of lines associated with the $v_7$–$v_9$ modes are likely due to a poor description of the mode mixing for these modes. For anti-CH$_3$OSO, the mode mixing is small and most intensity is with the $v_7$ mode, whereas for syn-CH$_3$OSO, the three modes are mixed, with $v_7$ approximately described as mainly CH$_3$ wagging, $v_8$ as S=O stretching mixed with CH$_3$ rocking, and $v_9$ as S=O stretching mixed with CH$_3$ wagging. All 11 modes predicted to have fundamental vibrational wavenumbers above 500 cm$^{-1}$, our detection limit, are observed in this work with relative intensities similar to predictions provides further support for the assignments of these lines in group A to syn-CH$_3$OSO. The assignments of two weak lines observed at 3028.4 and 1417.8 cm$^{-1}$ should be considered as tentative because the two weak lines predicted at 3019 ($v_1$) and 1442 ($v_5$) cm$^{-1}$ for syn-CH$_3$OSO has IR intensity less than 5 km mol$^{-1}$.

Syn-CH$_3$OSO and anti-CH$_3$OSO have similar vibrational wavenumbers, as listed in Table I. In our experiments, only one conformer appears to be observed because the observed lines show no splitting except the doublet at 1147.8 and 1147.4 cm$^{-1}$. If both conformers were present, the small differences in vibrational wavenumbers should result in several doublet lines for particular vibrational modes. Although we are unable to exclude positively the possibility of observed lines in group A being assigned to anti-CH$_3$OSO, we think that such an assignment is unlikely for the following reasons.

First, theoretical computations predict that syn-CH$_3$OSO is more stable than anti-CH$_3$OSO by $\sim$8 kJ mol$^{-1}$ (Refs. 6, 10, and 11); the syn-CH$_3$OSO should be dominant even at 300 K if we assume a Boltzmann distribution. The precursor CH$_3$OS(O)Cl also has a syn-form. Second, the average deviation of observed wavenumbers from the predicted anharmonic vibrational wavenumbers for syn-CH$_3$OSO (0.8%) is slightly smaller than that from predictions for anti-CH$_3$OSO (1.1%). For the two most intense lines, the observed lines at 989.7 and 714.5 cm$^{-1}$ are nearer those at 995 and 698 cm$^{-1}$ predicted for syn-CH$_3$OSO than those at 1017 and 727 predicted for anti-CH$_3$OSO. Third, according to theoretical calculations, among $v_7$ (S=O stretching), $v_8$ (CH$_3$ wagging), and $v_9$ (CH$_3$ rocking) modes of anti-CH$_3$OSO, only $v_7$ has substantial IR intensity, whereas for syn-CH$_3$OSO all three modes are mixed and have comparable intensities. Our observations agree better with the latter.

The observed lines in group A do not match those reported for CH$_3$OSO in solid p-H$_2$ at 1416.0, 1272.5, 1071.1, 917.5, and 633.8 cm$^{-1}$, nor do they match those of ClSO$_2$ in solid Ar or those predicted for ClOSO. Although two intense lines of CH$_3$OS(O)O, the product reported after photolysis of (CH$_3$O)$_2$SO at 248 nm, are predicted to have anharmonic vibrational wavenumbers (986 and 680 cm$^{-1}$) similar to those observed in group A (989.7 and 714.5 cm$^{-1}$), two additional intense lines predicted at 1261 and 1078 cm$^{-1}$ were unobserved in our experiments.

### B. Assignments of lines in group A in the CD$_3$OS(O)Cl/p-H$_2$ experiments to CD$_3$OSO

The deuterium-substitution experiment provides additional support for the assignment of lines in group A to syn-CH$_3$OSO. In Table II we compare the vibrational wavenumbers of lines in group A observed in the fully deuterated experiments with the harmonic and anharmonic vibrational wavenumbers of syn-CH$_3$OSO and anti-CH$_3$OSO computed quantum-chemically. To minimize the error of calculations, we also list the predicted values for syn-CH$_3$OSO in bracket in Table II. The predicted values are derived on multiplying...
the observed wavenumber of CH$_3$OSO with the isotopic ratio, defined as the ratio of calculated anharmonic vibrational wavenumber of the D-substituted species to that of natural CH$_3$OSO. Most deviations between observed and predicted vibrational wavenumbers are within 4 cm$^{-1}$ except for $\nu_7$ and $\nu_6$, which have deviations of 6 and 78 cm$^{-1}$, respectively. For the $\nu_7$ mode, the deviation might be due to different extents of mixing in CH$_3$OSO and CD$_3$OSO. The wavenumbers of $\nu_5$ and $\nu_6$ are similar. We made the assignments of $\nu_5$ and $\nu_6$ according to the relative intensity of $\nu_5$ and $\nu_6$; the latter is predicted to be much greater than the former. The wavenumber order of $\nu_5$ and $\nu_6$ is the reverse of that of predicted anharmonic vibrational wavenumbers, but agrees with that of harmonic vibrational wavenumbers. For the $\nu_6$ mode, the observed line at 1085.5 cm$^{-1}$ agrees with the predicted harmonic vibrational wavenumber of 1103 cm$^{-1}$. It is unclear why the correction of anharmonicity for this mode reduces this value to 1025 cm$^{-1}$; the reduction is much larger than typical corrections.

According to theoretical predictions, the $\nu_7$–$\nu_9$ modes of syn-CH$_3$OSO are mixed, with comparable intensities, whereas those of anti-CH$_3$OSO are less mixed, with the $\nu_7$ mode carrying the most intensity (Table I). In contrast, the $\nu_7$ mode of syn-CD$_3$OSO is predicted to carry the most intensity, whereas the $\nu_7$ mode of anti-CD$_3$OSO has more intensity than syn-CD$_3$OSO. Our observation of three lines at 1165.2, 1152.1, and 1147.8 cm$^{-1}$ with comparable intensities for CH$_3$OSO and a prominent line at 1159.7 cm$^{-1}$ for $\nu_7$ and weak lines at 920.1 and 889.0 cm$^{-1}$ for $\nu_8$ and $\nu_9$ modes of CD$_3$OSO strengthens the support for the assignments of lines in group A to syn-CH$_3$OSO/CD$_3$OSO.

In summary, we assigned lines in group A at 3028.4 cm$^{-1}$ to $\nu_1$ (CH$_2$ antisymmetric stretching), 2999.5 cm$^{-1}$ to $\nu_2$ (CH$_3$ antisymmetric stretching), 2950.4 cm$^{-1}$ to $\nu_3$ (CH$_3$ symmetric stretching), 1465.2 cm$^{-1}$ to $\nu_4$ (CH$_2$ scissoring), 1452.0 cm$^{-1}$ to $\nu_5$ (CH$_3$ deformation), 1417.8 cm$^{-1}$ to $\nu_6$ (CH$_3$ umbrella), 1165.2 cm$^{-1}$ to $\nu_7$ (CH$_3$ wagging), 1152.1 cm$^{-1}$ to $\nu_8$ (S=O stretching mixed with CH$_3$ rocking), 1147.8 cm$^{-1}$ to $\nu_9$ (S=O stretching mixed with CH$_3$ wagging), 989.7 cm$^{-1}$ to $\nu_{10}$ (C–O stretching), and 714.5 cm$^{-1}$ to $\nu_{11}$ (S–O stretching) modes of syn-CH$_3$OSO; the mode descriptions were made according to quantum-chemically predicted displacement vectors.

### C. Assignments of lines in group B in the CD$_2$OS(O)Cl/p-H$_2$ experiments to CD$_2$OH

As described in Sec. III, in experiments with CH$_3$OS(O)Cl/p-H$_2$, lines in group B observed at 3651.9, 3038.5, 1457.6, 1332.1, 1179.2, and 1047.0 cm$^{-1}$ agree well with those reported for CH$_3$OH in an Ar matrix at 3650, 1459, 1334, 1183, and 1048 cm$^{-1}$.

In experiments with CD$_3$OS(O)Cl/p-H$_2$, these lines shift to 3653.6, 2165.9, 1280.5, 1212.9, 1017.1, and 840.7 cm$^{-1}$. Although one would expect that CD$_2$OD would be the carrier, but the observed wavenumbers do not agree with the vibrational wavenumbers reported for CD$_2$OD in solid Ar at 2694, 1223, 1041, and 765 cm$^{-1}$.

Using the B3P86/aug-cc-pVDZ method, we computed anharmonic vibrational wavenumbers of CD$_2$OD to be 2715, 2400, 2203, 1013, 1029, 1234, and 756 cm$^{-1}$ for $\nu_1$–$\nu_7$, consistent with the literature experimental values as listed in Table III.

As shown in Table III, the observed wavenumbers and relative IR intensities agree satisfactorily with the anharmonic vibrational wavenumbers and IR intensities predicted for CD$_2$OH with the B3P86/aug-cc-pVDZ method. To
minimize the error of calculations, we also list the predicted values for CD$_2$OH in Table III. The predicted values are derived on multiplying the observed wavenumber of CH$_2$OH with the calculated isotopic ratio, defined as the ratio of the anharmonic vibrational wavenumber of CD$_2$OH to that of CH$_2$OH predicted quantum chemically.

D. Mechanism of formation and diminished cage effect in $p$-$H_2$

Lines of syn-CH$_3$OSO appear upon irradiation of the CH$_3$OS(O)Cl/p-$H_2$ matrix near 239 ± 20 nm. This behavior is consistent with a mechanism according to which, upon photolysis of CH$_3$OS(O)Cl to form Cl + CH$_3$OSO, some Cl atoms can escape from the original cage because of the diminished cage effect of $p$-$H_2$ so that CH$_3$OSO becomes isolated without a secondary reaction with the Cl atom. The presence of isolated Cl in $p$-$H_2$ is evident from the line at 943.8 cm$^{-1}$. The diminished cage matrix effect of $p$-$H_2$ makes feasible the production of CH$_3$OSO radicals from photolysis in situ of matrix-isolated CH$_3$OSO(Cl). Although the photolysis of purity (CH$_3$)$_2$SO at 248 nm yields CH$_3$ + CH$_3$OS(O)O, we observed no IR absorption line of CH$_3$OS(O)O in the CH$_3$OS(O)Cl/p-$H_2$ experiments; this might be due to either CH$_3$OS(O)O further decomposes or the yield is too small to detect.

The intensity of lines of syn-CH$_3$OSO decreases with further irradiation at the same wavelength because of dissociation of syn-CH$_3$OSO to produce CH$_3$ and SO$_2$, shown in Fig. 1(c) as a weak line at 624 cm$^{-1}$ for CH$_3$ and some lines near 1345 cm$^{-1}$ for SO$_2$. The SO and SO$_2$ fragments might react further with Cl atom to produce CISO$_2$ and CISO, respectively, as observed in our experiment in small quantities. Another possibility for the production of CISO$_2$ is that atomic Cl reacts with the SO$_2$ impurity. The SO$_2$ fragments might also react with CH$_3$ to produce CH$_3$SO$_2$.

Lines of CH$_3$OH also appeared upon irradiation of the CH$_3$OSOCl/p-$H_2$ matrix; their intensity increased with further irradiation. How CH$_3$OH was produced in a small proportion is unclear. The reaction of Cl with the CH$_3$OH impurity might produce CH$_3$OH. If this reaction is responsible for formation of CH$_3$OH in experiments of CH$_3$OS(O)Cl/p-$H_2$, CD$_3$OH rather than CD$_2$OD is expected to be produced in experiments of CD$_3$OS(O)Cl/p-$H_2$ because CD$_3$OH was employed in the synthesis of CD$_3$OS(O)Cl. In contrast, if photolysis of CH$_3$OSO would produce CH$_3$OH + SO$_2$, one would expect to observe CD$_2$OD from photolysis of CD$_3$OSO, inconsistent with our observation.

V. CONCLUSION

Photo irradiation near 239 nm of a CH$_3$OS(O)Cl/p-$H_2$ matrix at 3.2 K produced new features at 3028.4 (v$_1$), 2999.5 (v$_2$), 2950.4 (v$_3$), 1465.2 (v$_4$), 1452.0 (v$_5$), 1417.8 (v$_6$), 1165.2 (v$_7$), 1152.1 (v$_8$), 1147.8 (v$_9$), 989.7 (v$_{10}$), and 714.5 (v$_{11}$) that are assigned to syn-CH$_3$OSO. When a matrix of CD$_3$OS(O)Cl/p-$H_2$ was used, lines at 2275.9 (v$_1$), 2251.9 (v$_2$), 2083.3 (v$_3$), 1070.3 (v$_4$), 1056.0 (v$_5$), 1085.5 (v$_6$),
1159.7 (ν7), 920.1 (ν8), 889.0 (ν9), 976.9 (ν10), and 688.9 cm⁻¹ (ν11) were observed and are assigned to syn-CD2OSO; the mode numbers correspond to those used for syn-CH2OSO. These assignments are based on their photochemical behavior and a comparison of observed and calculated anharmonic vibrational wavenumbers, relative IR intensities, and D-isotopic shifts.

Four bands had been observed for gaseous CH3OSO.17 Our results are consistent with the five vibrational modes derived from simulation of rotational contours: 2991, 2956, 1159.7, 1245, 10-8

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