行政院國家科學委員會專題研究計畫 成果報告

間質隔離法之應用

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中華民國 年 月 日
In this 3-year project, we have published 8 papers so far, and 2 are under review. We have produced t-HSCO, OSCS, O(CS₂), and ONCO in matrices and assigned its IR absorption spectrum. We also determined the UV absorption spectrum of cyclic S₂O. A new pulse-deposition technique was developed for use of p-H₂ as a matrix host. We applied this technique and observed internal rotation of CH₃OH in solid p-H₂ for the first time. For absorption spectra of species of astronomical importance, we have determined absorption cross-sections of the B, C and D states of H₂O, HOD, and D₂O and made assignments. We also finished measurements of VUV absorption spectra of NH₃ and its isotopomers.

Keywords: matrix-isolation, isotopomers, Rydberg states

Disulfur oxide (denoted as SSO) isolated in solid Ar at 13 K was irradiated with light at 308 nm from a XeCl excimer laser. New lines at 799.1 (797.0), 574.9, and 544.1 (545.6) cm\textsuperscript{-1}, observed after photolysis, are assigned to cyclic S\textsubscript{2}O (denoted cyc-S\textsubscript{2}O) with $\angle$SOS $\cong$ 72.5$\pm$3.0$^\circ$ based on results of $^{34}$S- and $^{18}$O-isotopic experiments; lines in parentheses are associated with a minor matrix site and the broad line at 574.9 cm\textsuperscript{-1} may be deconvoluted to two lines at 575.4 and 574.6 cm\textsuperscript{-1}. Secondary photolysis at 248 nm diminishes lines of cyc-S\textsubscript{2}O and produces SSO. Theoretical calculations using MP2-FC and density-functional theories (BLYP and B3LYP) predict three stable isomers of S\textsubscript{2}O: cyc-S\textsubscript{2}O, SSO, and SOS, with the latter two having angular geometry. Relative energies, structures, vibrational wave numbers, and IR intensities were predicted for each isomer. According to calculations with B3LYP/aug-cc-pVTZ, cyc-S\textsubscript{2}O is bent with $\angle$SOS $\cong$73.3$^\circ$ and has the S-S bond (2.058 Å) and both S–O bonds (1.724 Å) elongated relative to those of SSO (1.909 and 1.474 Å, respectively); it lies 41.3 kcal mol\textsuperscript{-1} above SSO. Isomer SOS, 62.0 kcal mol\textsuperscript{-1} greater in energy than SSO, has length of S-O bonds 1.625 Å and $\angle$SOS $\cong$128.5$^\circ$. Calculated vibrational wave numbers, IR intensities, and isotopic shifts for cyc- S\textsubscript{2}O fit satisfactorily with experimental results. Two asymmetric transition states connecting SSO with SOS and cyc-S\textsubscript{2}O are characterized, yielding barriers for isomerization $\sim$104 and 122 kcal mol\textsuperscript{-1} (zero-point energy corrected), respectively. Photoconversion between angular SSO and cyc-S\textsubscript{2}O in a matrix cage is discussed. Cyc-S\textsubscript{2}O might be responsible for some distinct features in thermal emission from the surface of Io, Jupiter's moon.


The room temperature absorption spectra of water and its isotopomers D\textsubscript{2}O and HOD have been determined in absolute cross section units in the 125 to 145 nm wavelength region using synchrotron radiation. The experimental results for these $\tilde{B}$ band spectra are compared with results from quantum mechanical calculations using accurate diabatic \textit{ab initio} potentials. A Monte Carlo sampling over the initial rotational states of the molecules is applied in order to calculate the cross sections at a temperature of 300 K. The overall rotation of the water molecule is treated exactly. Both for the experimental and for the theoretical spectrum an analysis is made in terms of a component attributed to rapid direct dissociation processes and a component attributed to longer-lived resonances. The agreement between the results from experiment and theory is excellent for H\textsubscript{2}O and D\textsubscript{2}O. In the case of HOD in the results of theory two more resonances are found at low energy. It is demonstrated that the
width of the resonances of 0.04 eV is the result of overlapping and somewhat narrower resonances in the spectra of molecules differing in rotational ground state.


We employed pulsed deposition of p-H2 onto a cold target to form a matrix sample suitable for measurements of infrared absorption. Unlike the method of rapid vapor deposition at ~2.5 K, developed by Fajardo et al., this method can be performed at a temperature as high as 5.5 K, achievable with a closed-cycle refrigerator; pumping on liquid helium in a cryostat is eliminated. Compared with the enclosed-cell method developed by Oka, Shida, Momose, and coworkers, this method is more versatile in sample preparation, especially for samples at a greater concentration or with high reactivity. Two experiments were tested: the pulse-deposited sample of CH4/p-H2 yields an infrared absorption spectrum nearly identical to that recorded with rapid vapor deposition, and a sample of vinyl chloride (C2H3Cl) in solid p-H2 irradiated with laser emission at 193 nm yields C2H5, in contrast to formation of HCl, C2H2, and a complex of HCl-C2H2 observed upon photolysis of C2H3Cl in an Ar matrix. These experiments are also compared with those with n-H2 or Ne as the matrix host.


Irradiation of an Ar matrix sample containing H2S and CO (or OCS) with an ArF excimer laser at 193 nm yields trans-HSCO (denoted t-HSCO). New lines at 1823.3, 931.6, and 553.3 cm⁻¹ appear after photolysis and their intensity enhances after annealing; secondary photolysis at 248 nm diminishes these lines and produces OCS and CO. These lines are assigned to C–O stretching, HSC-bending, and C–S stretching modes of t-HSCO, respectively, based on results of ¹³C-isotopic experiments and theoretical calculations. Theoretical calculations using density-functional theories (B3LYP and PW91PW91) predict four stable isomers of HSCO: t-HSCO, c-HSCO, HC(O)S, and c-HOCs, listed in increasing order of energy. According to calculations with B3LYP/aug-cc-pVTZ, t-HSCO is planar, with bond lengths of 1.34 Å (H–S), 1.81 Å (S–C), and 1.17 Å (C–O), and angles ∠HSC ≅ 93.4° and ∠SCO ≅ 128.3°; it is more stable than c-HSCO and HC(O)S by ~9 kJ mol⁻¹ and more stable than c-HOCs by ~65 kJ mol⁻¹. Calculated vibrational wave numbers, IR intensities, and ¹³C-isotopic shifts for t-HSCO fit satisfactorily with experimental results. This new spectral identification of t-HSCO provides information for future investigations of its roles in atmospheric chemistry.

5. "Isomers of OCS₂: IR absorption spectra of OSCS and O(CS₂) in solid Ar", W.-J.

Irradiation of an Ar matrix sample containing O$_3$ and CS$_2$ with a KrF excimer laser at 248 nm yielded new lines at 1402.1 (1404.7), 1056.2 (1052.7), and 622.3 (620.5) cm$^{-1}$; numbers in parentheses correspond to species in a minor matrix site. Secondary photolysis at 308 nm diminished these lines and produced mainly OCS and SO$_2$. Annealing of this matrix to 30 K yielded a second set of new lines at 1824.7 and 617.8 cm$^{-1}$. The first set of lines are assigned to C=S stretching, O−S stretching, and S−C stretching modes of carbon disulfide S-oxide, OSCS, and the second set of lines are assigned to C=O stretching and OCS bending modes of dithiiranone, O(CS$_2$), respectively, based on results of $^{34}$S- and $^{18}$O-isotopic experiments and quantum-chemical calculations. These calculations using density-functional theory (B3LYP/aug-cc-pVTZ) predict four stable isomers of OCS$_2$: O(CS$_2$), SSCO, OSCS, and SOCS, listed in order of increasing energy. According to calculations, O(CS$_2$) has a cyclic CS$_2$ moiety and is the most stable isomer of OCS$_2$. OSCS is planar, with bond angles $\angle$OSC $\cong$ 111.9° and $\angle$SCS $\cong$ 177.3°; it is less stable than SSCO and O(CS$_2$) by ~102 and 154 kJ mol$^{-1}$, respectively, and more stable than SOCS by ~26 kJ mol$^{-1}$. Calculated vibrational wave numbers, IR intensities, $^{34}$S- and $^{18}$O-isotopic shifts for OSCS and O(CS$_2$) fit satisfactorily with experimental results.

6. "Intensities of vibration-rotational bands 3 − 0 to 6 − 0 of $^{14}$N$^{16}$O X $^2\Pi$, and an experimental evaluation of the radial function for electric dipolar moment", Y.-P. Lee, S.-L. Cheah, and J. F. Ogilvie, *Infrared Physics Tech.* (accepted).

We measured the strengths of individual line-like features, representing unresolved K doublets, in vibration-rotational bands 2−0 to 6−0 of 14N16O within each substate of electronic ground state X2P1/2,3/2 in mid and near infrared regions. Analyses of these data to derive values of matrix elements for vibrational transitions enabled production of a radial function for electric dipolar moment, containing seven parameters, that satisfactorily reproduces the intensities of about 700 such features for vibrational states up to m = 6.


molecule, are discussed. The effect of secondary photolysis on products is illustrated with formation of various conformers of HOONO from photolysis of HNO₃. The advantage of investigating electronic transitions that are difficult to observe in the gaseous phase and the mode and site selectivity of photodissociation for species in a matrix cage are also discussed. New developments involving use of p-H₂ as a matrix host, including the introduction of a pulse-deposition method for use at ~5 K and the exploration of internal rotation of larger molecules in solid p-H₂, are also presented.


Irradiation of a Ne matrix sample containing NO and CO near 4 K with an ArF excimer laser at 193 nm yielded new lines at 2045.1 and 968.0 cm⁻¹ that were depleted upon secondary photolysis at 308 nm. These lines are assigned to C=O stretching and mixed stretching modes of ONCO, based on results of ¹⁵N-, ¹³C,- and ¹⁸O-isotopic experiments and quantum-chemical calculations. These calculations using density-functional theory (B3LYP and PW91PW91/aug-cc-pVTZ) predict five stable isomers of NCO₂: ONCO, NCOO, N-cyc-CO₂, CNOO, and cyc-CNOO, listed in order of increasing energy. According to B3LYP calculations, ONCO has a trans configuration, with bond angles ∠ONC ≅ 136.3° and ∠NCO ≅ 160.7°. Calculated vibrational wave numbers, IR intensities, ¹⁵N-, ¹³C,- and ¹⁸O-isotopic shifts for ONCO agree satisfactorily with experimental results. ONCO was formed from reaction of CO with NO in its excited state.