

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(3/3)

計畫類別：整合型計畫

計畫編號：NSC93-2113-M-009-019-

執行期間：93年08月01日至94年07月31日

執行單位：國立交通大學應用化學系(所)

計畫主持人：李遠鵬

計畫參與人員：吳佳燕,楊勝凱,莊素琴

報告類型：完整報告

處理方式：本計畫可公開查詢

中 華 民 國 94 年 10 月 31 日

中文摘要

本三年計劃目前共發表 8 篇論文，另 2 篇送審中，預計尚可發表 2-4 篇，成果豐碩。在間質隔離法之應用方面，完成了 *t*-HSCO，OSCS，O(CS₂)，ONCO 之產生及其紅外吸收光譜診測，以及 *cyclic*-S₂O 之紫外光吸收光譜，並發展了使用 *p*-H₂ 為間質的脈衝沈積法且應用來首次觀測到 CH₃OH 在 *p*-H₂ 間質的內轉動。在星際重要分子之同位素光譜方面，完成了 H₂O，HOD，D₂O \tilde{B} 雷得堡態的測量及指認，也完成了 H₂O，HOD 及 D₂O 之 \tilde{C} 及 \tilde{D} 雷得堡態的測量和 NH₃ 及同位素之 VUV 和 IR 之光譜測量。

關鍵詞：間質隔離，同位素分子，雷得堡態

英文摘要

In this 3-year project, we have published 8 papers so far, and 2 are under review. We have produced *t*-HSCO, OCS, 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 \tilde{B} , \tilde{C} and \tilde{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

1. **"Ultraviolet absorption spectrum of cyclic S₂O in solid Ar"**, W.-J. Lo, Y.-J. Wu, and Y.-P. Lee, **J. Phys. Chem. A**, 107, 6944 (2003).

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⁻¹, observed after photolysis, are assigned to cyclic S₂O (denoted *cyc*-S₂O) with ∠SOS ≅ 72.5±3.0° based on results of ³⁴S- and ¹⁸O-isotopic experiments; lines in parentheses are associated with a minor matrix site and the broad line at 574.9 cm⁻¹ may be deconvoluted to two lines at 575.4 and 574.6 cm⁻¹. Secondary photolysis at 248 nm diminishes lines of *cyc*-S₂O and produces SSO. Theoretical calculations using MP2-FC and density-functional theories (BLYP and B3LYP) predict three stable isomers of S₂O: *cyc*-S₂O, 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*-S₂O is bent with ∠SOS ≅ 73.3° 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⁻¹ above SSO. Isomer SOS, 62.0 kcal mol⁻¹ greater in energy than SSO, has length of S-O bonds 1.625 Å and ∠SOS ≅ 128.5°. Calculated vibrational wave numbers, IR intensities, and isotopic shifts for *cyc*-S₂O fit satisfactorily with experimental results. Two asymmetric transition states connecting SSO with SOS and *cyc*-S₂O are characterized, yielding barriers for isomerization ~104 and 122 kcal mol⁻¹ (zero-point energy corrected), respectively. Photoconversion between angular SSO and *cyc*-S₂O in a matrix cage is discussed. *Cyc*-S₂O might be responsible for some distinct features in thermal emission from the surface of Io, Jupiter's moon.

2. **"Quantitative spectroscopic and theoretical study of the optical absorption spectra of H₂O, HOD, and D₂O in the 125-145 nm region"**, B.-M. Cheng, C.-Y. Chung, M. Bahou, Y.-P. Lee, L. C. Lee, R. Harrevelt, and M. C. Hemert, **J. Chem. Phys.** 120, 224 (2004).

The room temperature absorption spectra of water and its isotopomers D₂O 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 *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 H₂O and D₂O. 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.

3. **"Infrared matrix-isolation spectroscopy using pulsed deposition of *p*-H₂",** Y.-J. Wu, X. Yang, and Y.-P. Lee, **J. Chem. Phys.** 120, 1168 (2004).

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.

4. **"Isomers of HSCO: IR absorption spectra of *t*-HSCO in solid Ar",** W.-J. Lo, H.-F. Chen, Y.-J. Wu, and Y.-P. Lee, **J. Chem. Phys.** 120, 5717 (2004).

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.

Lo, H.-F. Chen, P.-H. Chou, and Y.-P. Lee, **J. Chem. Phys.** **121**, 12371 (2004).

Irradiation of an Ar matrix sample containing O₃ and CS₂ 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 SO₂. 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 dithiirane, O(CS₂), respectively, based on results of ³⁴S- and ¹⁸O-isotopic experiments and quantum-chemical calculations. These calculations using density-functional theory (B3LYP/aug-cc-pVTZ) predict four stable isomers of OCS₂: O(CS₂), SSCO, OSCS, and SOCS, listed in order of increasing energy. According to calculations, O(CS₂) has a cyclic CS₂ moiety and is the most stable isomer of OCS₂. OSCS is planar, with bond angles ∠OSC ≅ 111.9° and ∠SCS ≅ 177.3°; it is less stable than SSCO and O(CS₂) by ~102 and 154 kJ mol⁻¹, respectively, and more stable than SOCS by ~26 kJ mol⁻¹. Calculated vibrational wave numbers, IR intensities, ³⁴S- and ¹⁸O-isotopic shifts for OSCS and O(CS₂) fit satisfactorily with experimental results.

6. **"Intensities of vibration-rotational bands 3 – 0 to 6 – 0 of ¹⁴N¹⁶O X ²Π, 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 X²Π_{1/2,3/2} 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.

7. **"Preparation and Spectral Characterization of Novel Species in Matrices"**, Y.-P. Lee, **J. Chin Chem. Soc.** **52**, 641 (2005).

A review of matrix-isolation experiments performed in this laboratory for the past thirteen years (1992–2004) is given; the work emphasizes the preparation and spectral characterization of novel species of atmospheric interest, and the significance of detection of some species is discussed. A previous review (*J. Chin. Chem. Soc.* **1992**, 39, 503) covers work from 1981 to 1991. Various methods for production of novel species, including reaction in the gaseous phase, laser photolysis of a single precursor *in situ*, reaction of a molecule with an atom or radical in a matrix cage and reaction of a molecule with an electronically excited

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.

8. **"Isomers of NCO₂: IR absorption spectra of ONCO in solid Ne"**, Y.-J. Wu and Y.-P. Lee, **J. Chem. Phys. (in press)**

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.