國 立 交 通 大 學

應 用 化 學 系

博 士 論 文

尖端紅外光譜法的應用:

Ⅰ. 以紅外–真空紫外光游離法研究甲醇團聚物及甲基硫自由基

Ⅱ. 以霍式紅外光譜法研究二甲氨基苯腈及聚甲基丙烯酸甲酯之電致吸收

Applications of Frontier Infrared Spectroscopy:

I. Infrared-Vacuum Ultraviolet Photoionization Studies on Methanol Clusters and CH_3S Radicals

II. Vibrational Stark Spectral Studies on DMANB and PMMA

研 究 生：韓慧玲 (Hui-Ling Han)

指導教授：李遠鵬 教授 (Prof. Yuan-Pern Lee)

中華民國一百年七月

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Abstract

Using a broadly tunable infrared (IR) optical parametric oscillator laser and a vacuum ultraviolet (VUV) laser together time-of-flight (TOF) mass spectrometry, we demonstrate (1+1) IR-VUV photoionization that (IR-VUV-PI) and IR depletion-VUV ionization methods have an advantage over conventional IR-absorption techniques for vibrational spectroscopy of free radicals and neutral clusters.

We investigated IR spectra of size-selected methanol clusters ($(CH_3OH)_n$ with n = 2−6) in a pulsed supersonic jet in the CH- and OH-stretching regions using the IR depletion-VUV ionization technique. VUV emission at 118 nm served as the source of ionization in a time-of-flight mass spectrometer. The tunable IR laser emission served as the source of vibrational predissociation prior to ionization. The variations in intensities of protonated methanol cluster ions $(CH_3OH)_nH^+$ (n = 1−5), CH_3OH^+, and $(CH_3OH)_2^+$ monitored as the IR laser light was tuned across the range 2650−3750 cm^{-1} were recorded as the action spectra. Careful processing of these action spectra base on a simple dissociation mechanism yielded IR spectra of the size-selected methanol clusters.

With IR-VUV photoionization method, we investigated the IR spectrum of mass-selected CH_3S radicals in the range 2790−3270 cm^{-1}. CH_3S was produced from photodissociation at 248 nm of CH_3SH in a supersonic jet. CH_3S^+ ions were produced with (1+1) IR-VUV photoionization and detected with the time-of-flight technique. The IR spectrum of CH_3S was obtained on maintaining the wavelength of the VUV laser at 134.84 nm and tuning the wavelength of the IR laser while monitoring the change in intensity of the CH_3S^+ signal. The advantage of the mass-selective detection enables us to obtain the IR spectrum of CH_3S radical showing absorption bands with no interference from the precursor. Our results provide direct evidence for the assignments of ν_1 and ν_4 modes of gaseous CH_3S.

Vibrational Stark spectra provide information about the electrical properties of molecules in liquids that are otherwise difficult to access; this property also makes possible a local probe of electrostatic fields in a protein system. We constructed a system for vibrational Stark spectroscopy that is capable of measuring infrared absorption, induced with an electric field, of a poly(methylmethacrylate) (PMMA) film with great sensitivity; the system is capable of detection of relative changes as small as 4×10^{-6} in the mid-infrared region. With this system, we investigated the effects of an external electric field on IR absorption spectra of 4-(N,N-dimethylamino) benzonitrile (DMABN) in a PMMA film. The electric-field-induced change in each vibrational line is reproduced with a superposition of the IR absorption spectrum, its first and second derivatives. The results indicate that the electric dipole moments and the molecular polarizabilities of the upper and lower states of DMABN differ from those of PMMA. The difference in the dipole moment, $|\Delta\mu|$, for the C=O stretching mode at 1732 cm^{-1} of PMMA and for the C≡N stretching mode at 2213 cm^{-1} of DMABN are determined to be 0.016 and 0.012 D/*f*, respectively, and the difference in the molecular polarizabilities, $|\Delta\alpha|$, are determined to be 0.19 and 2.33 A^3/f^2, respectively. The large alteration of polarizability of the C=O stretching and of the C-O-C stretching modes of PMMA might indicate that the side chains are oriented significantly in the presence of an electric field. Such a field induced orientation might induce a dielectric polarizability that yields large change in polarizability.

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韓慧玲

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