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Progress Report For FY 1989 DE-FG03-89ER14066

[High-resolution Raman spectroscopy of and clusters in molecula

(a) Technical progress

With DoE funds we have purchased a Spectra-Physics GCR-3 Nd:YAG laser to be used in ionization-detected stimulated Raman spectroscopy (IDSRS) and Fourier transform-IDSRS experiments. (I shall refer to the two types of IDSRS schemes as ionization-gain stimulated Raman spectroscopy - IGSRS - and ionization-loss stimulated Raman spectrosocpy - ILSRS.) The laser has been delivered. It has not been used yet, however, because having acquired additional money in the form of matching funds from UCLA, we have decided to get the laser injection-seeded. This is being done at this time. We expect delivery and installation within three weeks. The addition of this laser to the existing IDSRS apparatus represents a very significant step forward in capabilities. It will allow (1) direct time domain studies of vibrational dynamics and dissociation (nsec timescale), (2) survey spectral domain studies to be performed at reasonable resolution, (3) greater signal averaging capabilities (30 Hz repetition rate vs. 10 Hz), and (4) a very significant reduction in noise (as much as a factor of ten) due to the injection seeding.

In order to render our existing 10 Hz Nd:YAG laser system compatible with the new laser it was necessary to upgrade the old laser from 10 to 30 Hz. This has already been accomplished.

DoE funds have been used to purchase a Spectra-Physics WEX apparatus to allow the generation of high power tunable ultraviolet from 220 to 430 nm by frequency doubling and mixing in nonlinear crystals. The WEX is operational.

We have acquired a small, fast computer for data collection and analysis with DoE funds. The computer, operational for several months, has reduced our FT-IDSRS analysis time by a factor of about ten.

We have succeeded in implementing a He-Ne laser-calibrated interferometer in FT-IDSRS experiments. We now use this interferometer routinely. It represents several orders of magnitude improvement over our original interferometer set-up in terms of line position accuracy, noise levels, elimination of "ghosts", and available frequency range. We are currently constructing a more sophisticated interferometer that will allow for resolution in the 0.002 cm^{-1} range.

The entire apparatus for the proposed resonantly enhanced FT-coherent Raman spectroscopy (FT-CRS) experiments - a picosecond laser system and molecular beam apparatus - has been put together (primarily with NSF funds). The apparatus is currently operational in other types of studies but will be available for FT-CRS experiments within the next year.

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(b) Scientific progress

Most of the experiments performed to date have pertained to IDSRS and FT-IDSRS studies of benzene complexes and clusters. Some of this work is described in a paper soon to be submitted to J. Opt. Soc. Am. B.

A great deal of our effort has been focused on the Raman spectroscopy of benzene dimer and isotopically substituted dimers in the region of the ν_1 totally symmetric C-C stretch fundamental. The following is a summary of what we have learned. (1) We have found that the ν_1-excited d_0-d_0 species (d_0 represents C_6H_6 and d_6 represents C_6D_6) lives for nsec or longer, as does d_0-d_6 subsequent to ν_1 excitation of the d_0 moiety . However, ν_1-excited d_6-d_6, and d_0-d_6 with the d_6 moiety excited, live for significantly shorter times, despite the fact that the d_0-excited species have 50 cm^{-1} more energy than the d_6-excited species. We believe this behavior is reflective of the fact that the ν_1 vibrational motion in the d_6 moiety has significantly more carbon-hydrogen stretching character than the ν_1 motion in the d_0 moiety does. (2) Raman specta in the ν_1 region of d_0-d_0 obtained by FT-IGSRS and FT-ILSRS (0.05 cm^{-1} resolution) show the ν_1 resonance to be split into three different resonances. We have found that these different resonances are associated with vibrationally excited states that have significantly different lifetimes, despite the fact that the resonances all occur within 1.5 cm^{-1} of one another. Moreover, we find that the two major resonances are associated with markedly different vibronic spectra. The evidence seems to point to the existence of two different conformers of d_0-d_0 existing in the molecular beam. Further experiments to examine this are under way. (3) We have accurately measured ν_1 vibrational frequencies for d_0-d_0, d_0-d_6, and d_6-d_6. We find the major homodimer resonances to be significantly red-shifted (about 0.5 cm^{-1}) with respect to benzene monomer resonances. In contrast, the two d_0-d_6 resonances are shifted by less than 0.1 cm^{-1} from the appropriate monomer values. This behavior is analogous to the shifts of vibronic resonances in benzene dimers and probably reflects the excitation exchange interaction energy existing in the homodimers but absent in the heterodimer.

In addition to benzene dimers we have also studied higher benzene clusters - i.e., the trimer and tetramer. Like the dimer, we find that the trimer lives for nanoseconds or longer upon ν_1 excitation, based upon our observation of a significant IGSRS signal. The ν_1 excited tetramer appears not to live as long, given the absence of an IGSRS signal for it. High resolution (0.05 cm^{-1}) Raman spectra have been obtained for both species. The trimer exhibits just one strong ν_1 resonance at a shift of about 1.4 cm^{-1} from the monomer value. The tetramer appear to exhibit two resonances, both slightly to the blue of the trimer resonance. The observed linewidth of each of these resonances is resolution (0.05 cm^{-1}) limited.

Mixed one-to-one complexes of benzene with atoms or molecules have also been studied. ν_1 line position shifts of benzene-Ar, benzene-N_2, benzene-CH_4, and others have been measured.

Each of these species upon ν_1 excitation lives for nsec or longer, despite the fact that the vibrational excitation is significantly higher in energy than that required to dissociate these weakly bound species. In conjunction with the study of benzene-N_2 and benzene-phenol, we have demonstrated that it is possible with ILSRS (or FT-ILSRS) to study the vibrational spectroscopy of solvent species in solute-(solvent)$_n$ complexes, even though probe photoionization proceeds through a solute-localized transition. For instance, we have measured Raman spectra of benzene-N_2 in the region of the N_2 stretching fundamental and have obtained the position of the N_2-localized vibrational transition for the complex. Similarly, for benzene-phenol, we have observed Raman resonances corresponding to both the phenol and benzene moieties.

Future Plans

(a) Apparatus

With UCLA matching funds and other monies we shall purchase a Spectra-Physics PDL-3 dye laser. The laser, which has 0.05 cm^{-1} bandwidth, will be used in the IDSRS experiments. It will allow for 0.05 cm^{-1} resolution survey Raman spectra, or if used as the probe laser will allow for similar resolution in the vibronically resonant probe process. In addition, the availability of three lasers will allow two-color photoionization probe schemes in IDSRS to be implemented.

We plan to complete construction of the HeNe controlled interferometer that will allow for 0.002 cm^{-1} Raman resolution.

(b) Experiments

Much work remains to be done on benzene clusters. We shall measure vibrational lifetimes directly in the time-domain. In cases where this is not possible, we shall obtain high resolution spectral domain data to place lower limits on vibrational lifetimes. Such experiments will surely be performed for the dimers, trimer, and tetramer in the 1000 cm^{-1} (ν_1) and 3000 cm^{-1} (ν_2) regions. We have thus far performed no Raman studies in the ν_2 region of the benzene clusters. We plan on doing so in the next year. We are also planning to try to measure Raman spectra of even higher clusters of benzene. We hope to see manifestations of the structure (via line positions and the splitting of resonances) and stability (via linewidths) of these clusters as a function of cluster size.

We plan to form solute-$(\text{solvent})_n$ clusters and study via (FT)-ILSRS the vibrational spectroscopy of both the solute and the solvent species. In these studies of systems we hope to probe the structure and dynamics of these microsolvated species. Likely candidates include benzene-$(N_2)_n$, benzene-$(CH_4)_n$, phenol-$(H_2O)_n$, and phenol-$(MeOH)_n$.

Numerous ILSRS survey Raman studies of molecules and complexes are planned with the aim of obtaining background spectroscopic information as a preliminary to performing high resolution studies. In this regard we will study species with torsional degrees of freedom (toluene, for example) and some other cluster systems (naphthalene clusters, for example).

We plan to implement resonance-enhanced FT-CRS studies within the next year. We shall work toward performing high resolution pure rotational Raman spectroscopy with the aim of learning about the equilibrium geometries of large molecules, complexes and clusters.

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