LETTERS TO THE EDITOR

COMMUNICATIONS

Two-photon spectroscopy of ultracold large molecules in planar supersonic expansions

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The currently available information concerning two-photon (TP) molecular spectra of large molecules[1-4] is still inherently limited. The solution spectra[4,5] are practically devoid of vibrational structure, the gas phase spectra[4] suffer from rotational broadening, and vibrational sequence congestion, while low temperature, high-resolution crystal spectra[6,7] are complicated by site splittings, inhomogeneous broadening, and phonon side-structure. The well-resolved, electronic–vibrational TP spectra of "isolated," large molecules will be of considerable interest. The interrogation of such TP spectra requires effective rotational–vibrational cooling, which can be accomplished by the utilization of seeded supersonic expansions.[8] The multiphoton ionization technique was applied[9,10] for TP spectroscopy of benzene and some of its derivatives cooled in supersonic expansions. The low local densities ($\rho \sim 10^{12}$–10^{13} cm^{-3}) of the seeded, ultracold, large molecules encountered at the interrogation distance x for a conventional supersonic expansion (where $\rho \propto x^{-2}$)[11] may prohibit the application of the fluorescence excitation method, which will not be sufficiently sensitive for the detection of TP transitions. We have developed a pulsed planar supersonic source,[12] which was utilized for internal cooling of large molecules. In the linear supersonic jet $\rho \propto x^{-1}$, resulting in high densities, ($\rho \sim 10^{14}$ cm^{-3}) of ultracold molecules, whose TP excitations are amenable to experimental interrogation. We wish to report the observation of a high resolution, two photon, vibronic spectrum of the ultracold fluorene ($C_{13}H_{10}$) molecule in a planar supersonic expansion.

A pulsed, planar, supersonic beam source was constructed from two spinning concentric cylinders.[12] Slits of dimensions $L = 0.2$ mm wide and 35 mm long were machined in the internal cylinder (length 70 mm, diameter 20 mm, wall thickness 0.5 mm) and in the external cylinder, whose i.d. matched the o.d. of the internal cylinder within a tolerance of 0.05 mm. The outer wall of the moving internal cylinder was lubricated with MoS_2 powder. A sample fluorene was placed near the inner cylinder, heated to 100 °C (vapor pressure ~1
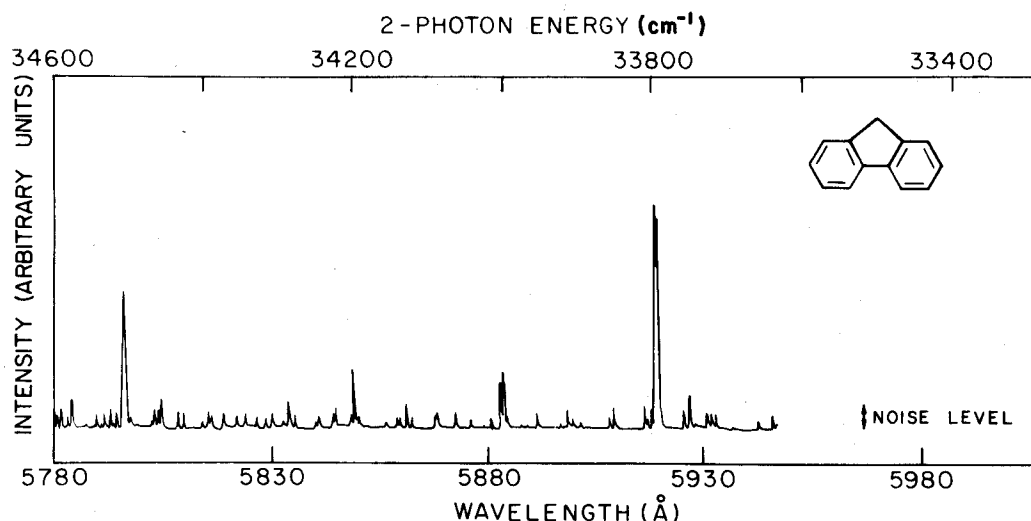

FIG. 1. Two-photon fluorescence excitation spectrum of fluorene cooled in a pulsed planar supersonic expansion. The fluorene was heated to 100°C (vapor pressure ~1 Torr) and seeded into Ar at $p = 90$ Torr. The seeded gas was expanded through a 0.20 × 35 mm slit. The dye laser in the spectral range 5780–5980 Å, with a spectral width of 0.3 cm^{-1}, was focused by a 70 mm lens, passed by a Pyrex glass and imaged at a distance of 6 mm from the slit at the center of the slit. The noise level corresponds to one-photon signals of the photomultiplier dark current and/or to laser stray light.
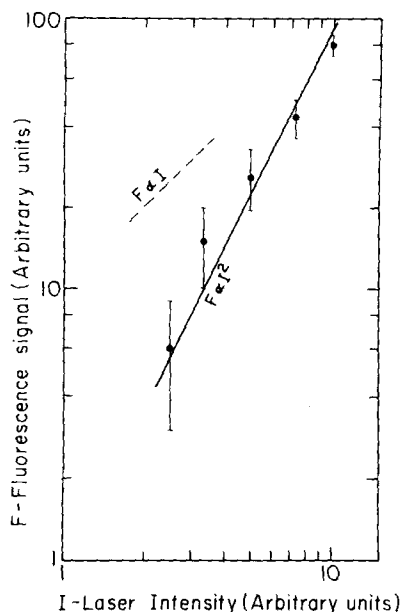
FIG. 2. The dependence of the intensity of the molecular fluorescence excited at 5920.0 Å, which corresponds to the two-photon excited electronic origin of the $^1A_1 \rightarrow {}^1B_2$ transition on the laser intensity. The two straight lines represent the planar dependence $F \propto I$ (dashed line) and the quadratic $F \propto I^2$ dependence (solid line). The experimental data obey the superplanar relation $F \propto I^n$, where $n \simeq 2$.

Torr) and mixed with Ar in the pressure range $p = 20-150$ Torr, which was fed into the inner cylinder. The pulsed planar seeded supersonic jet was characterized by a repetition rate of ~12 Hz and a pulse width of 150 μsec. Light from a pulsed nitrogen pumped Rhodamine 6G dye laser (spectral width of 0.3 cm^{-1}, pulse duration 4×10^{-9} sec, pulse energy ~ 50 μJ) was focused by a lens (focal length 70 mm), passed through a Pyrex filter, and imaged on the supersonic expansion at the distance $x = 6$ mm ($x/L = 30$) from the source. The temporal coincidence between the laser pulses and the supersonic gas pulses was achieved using an IR optical switch (Spectronix 1874-14) and a home-made variable delay unit. The fluorescence in the range 2900-4000 Å was filtered by a UV short-pass filter, detected by a photomultiplier, and recorded by a boxcar integrator. This detection system was limited by one-photon signals of dark current and/or laser stray light, which correspond to the noise level marked in Fig. 1.

Figure 1 shows the TP fluorescence excitation spectrum of fluorene excited in the spectral region 5780-5980 Å with the corresponding TP energies being in the range 33 400-34 600 cm^{-1}. Four spectral features (with a signal/noise ratio exceeding 3) were identified in this TP spectrum. The lowest energy spectral feature excited at 5920.0 Å (TP energy 33 783 cm^{-1}) is assigned to the TP excitation of the origin (0-0) of the lowest spin-

allowed electronic $^1A_1 \rightarrow {}^1B_2$ transition of fluorene.[13,14] The TP energy of the electronic origin coincides with the energy of 33 783 cm^{-1} (2960.0 Å) for the 0-0 of the $^1A_1 \rightarrow {}^1B_2$ one-photon transition of fluorene in a supersonic expansion.[11] The width (FWHM) of the origin in the TP spectrum is 3.5 ± 0.5 cm^{-1}, being due to unresolved rotational structure. In Fig. 2 we portray the dependence of the fluorescence intensity F at the electronic origin on the laser intensity I, which exhibits the superplanar $F \propto I^2$ relation, as is appropriate for TP excitation. An approximate estimate of the TP absorptivity,[3] δ at the electronic origin of ultracold fluorene results in $\delta \approx 3 \times 10^{-46}$ cm^4 sec photon^{-1}. Such a magnitude of δ corresponds to an allowed TP molecular transition.[3] Three additional spectral features excited at 5884.0, 5849.4, and 5975.0 Å, which correspond to the TP energies of 207 ± 4, 408 ± 4, and 727 ± 4 cm^{-1} above the electronic origin, are assigned to a_1 vibrations in the $^1B_2$ state. The same prominent a_1 vibrations are revealed in the one-photon spectra of fluorene in crystals,[14] heptane matrix,[14] and supersonic expansions.[13] The low (C_{2v}) symmetry of the fluorene molecule renders identical vibronic features to be allowed, both in the conventional one-photon spectroscopy and in the TP spectra.[3-5]

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