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ABSOLUTE RATE MEASUREMENTS OF TWO-PHOTON PROCESS OF GASES, LIQUIDS, AND SOLIDS

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Due to rapid improvements in high-power laser performance, two-photon absorption processes have become a very useful tool for studying the molecular structures of various gases, liquids and solids. However, measurements of absolute two-photon absorption cross sections were more or less ignored previously because of their small size. In this work, we obtained not only the two-photon absorption spectra, but also measurements of their absolute cross sections for various gases, liquids, and solids.

Resonance ionization spectra with the two-photon absorption process to various excited states for Ar, Kr,^{1,2} H₂, Xe,³ NO, CO,⁴ and ArNO were obtained. By combining a coherent vacuum ultraviolet (VUV) beam; which was produced by a third harmonic generation process in a Xe cell, two-photon absorption and three-photon ionization spectra for Ar, Kr, and H₂ were obtained. Another process combining either two ultraviolet (UV) or one UV photon plus one visible photon was used for exciting various states of Xe, CO, NO, and ArNO. Vibronic state-selected molecules and van der Waals molecules were produced by a rare gas seeded nozzle beam. A mass spectrometer was used to detect the ions by resonance ionization spectroscopy (RIS).

The experimental schematic for two-photon resonance excitation of CO is shown in Fig. 1. The two-photon absorption process promotes $\text{CO}(X^1\Sigma^+)_{v=0}$ to $\text{CO}(A^1\pi)_{v=1}$, a blue laser beam excites $\text{CO}(A^1\pi)_{v=1}$ to $\text{CO}(B^1\Sigma^+)_{v=0}$. The

$\text{CO}(B^1\Sigma^+)$ molecules can be ionized by the UV beam which proceeds the two-photon excitation. The two-photon absorption cross section of $\text{CO}(X)_{v=0} \rightarrow \text{CO}(A)_{v=1}$ obtained was $2.2 \times 10^{-47} \text{ cm}^4 \text{ sec mol}^{-1}$ and the ionization cross sections of $\text{CO}(B^1\Sigma^+)_{v=0}$ was determined to be $1.4 \times 10^{-20} \text{ cm}^2$. Molecular term energies for these two transitions were determined as follows:

$$\Delta E(J, J') = 66227.9 + 1.577J'(J' + 1) - 0.346J(J + 1)$$

for

$$\Delta E(J', J'') = 20688 + 1.948J''(J'' + 1) - 1.577J'(J' + 1)$$

for

Similar types of experiments were also performed in other gases.

Two-photon induced fluorescence spectra were obtained to study the excitation and decay mechanism for dyes,⁵ neat benzene, toluene, xylene isomers, and polysubstituted methyl benzenes. By measuring the absolute number of fluorescent photons, two-photon absorption cross sections and two-photon induced fluorescence cross sections for aromatic compounds were obtained. The results are shown in Table I.

In addition, two-photon induced fluorescence spectra of various alkali halide crystals were obtained,^{6,7} and the mechanism for formation and decay of V_K centers as well as F-centers were studied. The two-photon absorption cross sections and the fluorescence yields due to two-photon absorption were measured.

The formation of F-centers for certain alkali halide crystals can be conveniently used to determine the band gaps of these crystals.⁸

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REFERENCES

1. M. P. McCann, C. H. Chen, and M. G. Payne, Appl. Spectrosc. 41, 399 (1987).
2. M. P. McCann, C. H. Chen, and M. G. Payne, Chem. Phys. Lett. 138, 250 (1987).
3. C. H. Chen, G. S. Hurst, and M. G. Payne, Chem. Phys. Lett. 75, 473 (1980).
4. W. R. Ferrell, C. H. Chen, M. G. Payne, and R. D. Willis, Chem. Phys. Lett. 97, 460 (1983).
5. C. H. Chen and M. P. McCann, Opt. Commun. 63, 338 (1987).
6. C. H. Chen, M. P. McCann, and J. C. Wang, Solid State Commun. 61, 559 (1987).
7. C. H. Chen and M. P. McCann, Chem. Phys. Lett. 126, 54 (1986).
8. C. H. Chen and M. P. McCann, Opt. Commun. 60, 196 (1986).

Figure 1. Data acquisition scheme. The two dye lasers are pumped by a Lumonics Nd:YAG laser. The "doubler" is the KDP crystal with appropriate red filter.

Table I. Two-photon absorption cross sections (δ) and two-photon induced fluorescence cross sections (δ_F) for benzene, toluene, and xylene. The unit of δ and δ_F is $\text{cm}^4 \text{ sec mol}^{-1} \text{ photon}^{-1}$.

Photon wavelength (nm)	Benzene		Toluene		o-xylene		m-xylene	
	δ	δ_F	δ	δ_F	δ	δ_F	δ	δ_F
<1.0	(-51)							
3.4	(-52)*	1.4 (-54)						
8.2	(-52)*	3.3 (-54)	5.4 (-53)**	6.0 (-55)				
2.0	(-51)							
8.7	(-50)		1.2 (-52)**	1.3 (-54)				
1.0	(-51)	1.7 (-51)						
6.0	(-52)*	2.5 (-54)			2.1 (-51)***	2.1 (-53)	1.2 (-51)***	1.6 (-53)
2.5	(-52)*	1.0 (-54)	1.1 (-52)**	1.2 (-54)				
					2.1 (-51)***	2.1 (-53)		
							1.2 (-51)***	1.6 (-53)
			3.6 (-52)**	4.0 (-54)				
					5.0 (-52)***	5.0 (-54)	3.1 (-52)***	4.0 (-54)
1.24	(-49)*	5.0 (-51)	1.0 (-49)**	1.1 (-51)			3.0 (-49)***	4.0 (-51)

- represents δ obtained from the assumption of η_F of benzene is 0.004
- represents δ obtained assuming η_F is 0.011 for toluene
- represents δ obtained by the assumption of η_F equal to 0.01, 0.013, and 0.01 for o-xylene, and m-xylene, respectively.