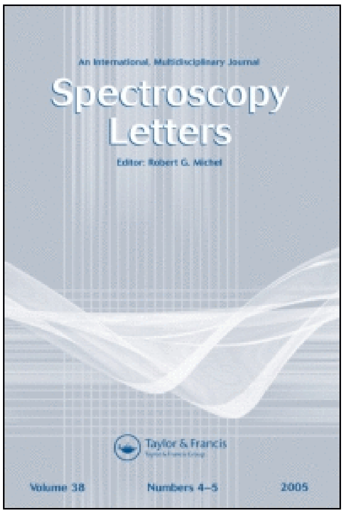

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

On the Resonant Raman Spectrum and the Excitation Profile of the Charge-Transfer Molecular Adduct between $(CH_3)_2S$ and Iodine

Rosario Sergio Cataliotti[a]; Giulio Paliani[a]; Sergio Santini[a]
[a] Dipartimento di Chimica, Laboratorio di Chimica Fisica dell'Università, Perugia, Italy

To cite this Article Cataliotti, Rosario Sergio , Paliani, Giulio and Santini, Sergio(1983) 'On the Resonant Raman Spectrum and the Excitation Profile of the Charge-Transfer Molecular Adduct between $(CH_3)_2S$ and Iodine', Spectroscopy Letters, 16: 6, 455 — 461

To link to this Article: DOI: 10.1080/00387018308062365

URL: http://dx.doi.org/10.1080/00387018308062365

SPECTROSCOPY LETTERS, 16(6), 455-461 (1983)

On the Resonant Raman spectrum and the excitation profile of the charge-transfer molecular adduct between $(CH_3)_2S$ and Iodine.

by Rosario Sergio Cataliotti*, Giulio Paliani and Sergio Santini

Dipartimento di Chimica, Laboratorio di Chimica Fisica dell'Università, Via Elce di Sotto, 8 - 06100 Perugia, Italy.

Abstract

Resonance Raman spectrum of the molecular complex between $(CH_3)_2S$ and Iodine in CCl_4 is reported. The resonance enhanced Raman peaks have been studied as a function of the exciting laser frequency and the RR excitation profiles (RREP) have been derived. Peculiar features in such RREP curves are presented and discussed.

Resonant Raman Spectroscopy (RRS) has been used in the last few years in order to obtain information on the excited electronic states of various molecules [1-5]. This information is normally derived from the study of the excitation profiles (intensity of the RR lines, versus the frequency of the exciting laser lines), and is referred to the lifetimes of the excited states, to the geometry of these states, to the vibronic coupling process, etc. [6,7].

---

* to whom correspondence should be addressed.

0038-7010/83/1606-0455$3.50/0

Studies on the Iodine molecule have become an object of actual interest [8-11] because this molecule is being used as an impurity in the doping of some organic semiconductors like, for example, polyacetylene. The role played by I_2 in the excited state of the molecular interaction state of these systems is not yet well understood. It cannot be excluded however, that the state of molecular interaction is a charge-transfer state where I_2 participates as an acceptor of electronic charge.

Organic sulphur compounds give rise to very stable charge-transfer complexes with iodine as the acceptor and have "inter alia" large and intense electronic absorption maxima between 400 and 500 nm [12-15].

It is possible therefore to excite the RR spectrum with commercial ion lasers having Argon as the exciter.

The aim of this note is to present some preliminary results we have now obtained on the RR spectrum of the molecular adduct between $(CH_3)_2S$ and I_2 in carbon tetrachloride.

The excitation profiles of the lines at 535 (ν_1), 614,5 (ν_2) and at 1087,5 (ν_3) of the $(CH_3)_2SI_2$ complex in carbon tetrachloride were determined using an HG 2S Jobin Yvon Raman spectrometer equipped with a Spectra Physics Model 164-06 Argon laser, SEA photon counting electronics and a Laben Model 8004 multichannel analyser. All spectra were run using a rotating cell, the laser beam being collimated at the edge of the cell, in order to avoid back absorption by the sample of scattered photons. The laser power was 45 mW at the sample and the spectral slit width was 18 cm^{-1}. The intensities of the ν_1, ν_2 and ν_3 lines were measured from peak heights relative to the 459 cm^{-1} line of CCl_4 and corrected using the relationship:

$$S = \left[I(\nu)/I_o(\nu_o)\right](\nu_o/\nu)^4$$

where $I(\nu)$ is the peak height of the relevant RR line at

Table 1 - Corrected relative intensities (S) of the RR lines of $(CH_3)_2SI_2$ for different laser lines$^{a)}$

Laser line (nm)	Fundamental ν_1	ν_2	ν_3
514.5	0.68±0.06	0.81±0.04	0.59±0.05
501.7	0.66±0.05	0.76±0.02	0.57±0.03
496.5	0.69±0.02	0.88±0.03	0.56±0.03
488.0	0.81±0.03	1.00±0.04	0.84±0.03
476.5	0.73±0.02	0.80±0.04	0.73±0.02
472.7	0.77±0.08	0.88±0.08	0.74±0.08
465.8	0.79±0.09	0.92±0.08	0.85±0.09
457.9	1.00±0.05	0.98±0.05	1.00±0.04

a) The most intense line for each fundamental mode was assigned an intensity of unity. The uncertainty limits are one standard deviation.

the frequency, ν, $I_o(\nu_o)$ is the peak height of the solvent line, used as internal standard, at frequency ν_o. The intensities relative to unity for the three lines are given in table 1.

The visible electronic spectrum of $(CH_3)_2SI_2$ was measured at a concentration of 2.10^{-4}M of the complex in CCl_4, using a Perkin-Elmer Model 572 Coleman spectrophotometer and cells of 10 mm path length.

Fig. 1 shows the RR spectrum in CCl_4 of the adduct recorded with the 4880 Å radiation of the Argon laser. Fig. 2 shows the electronic absorption and part of its RR excitation profile. This part is the one which it was possible to obtain with the eight lines available with our laser. It is apparent from Fig. 2 that the RREP curves of the resonance-enhanced ν_1, ν_2 and ν_3 lines of the Raman resonant spectrum follow the low

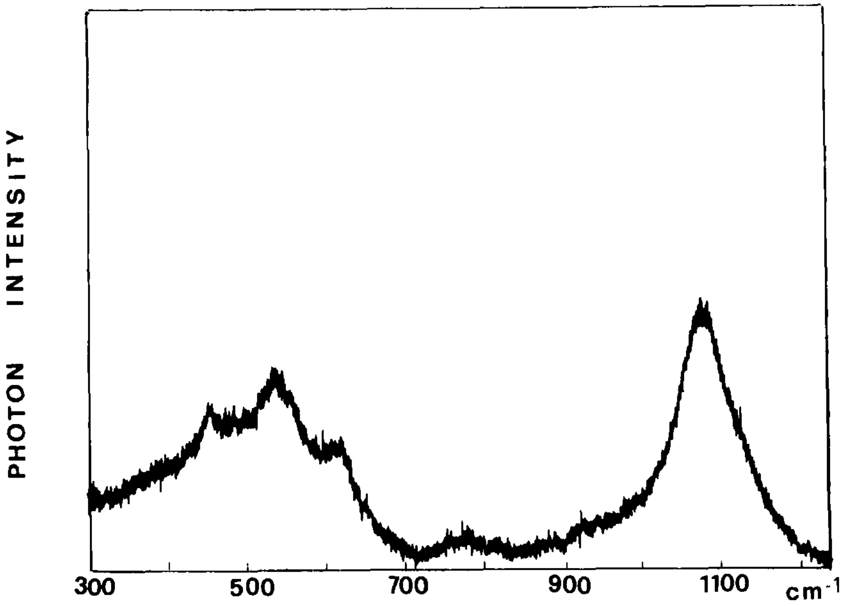

Fig. 1 - Resonant Raman Spectrum of $(CH_3)_2SI_2$ in CCl_4

frequency side of the absorption curve of the adduct quite well, as it is expected if the resonance conditions are attained.

The vibrational spectrum of the donor Dimethylsulphide has been reported by various authors [16-19]. When the adduct is formed, even if the donor is used in large amounts in order to stabilize the charge-transfer interaction and avoid free I_2 at the equilibrium, no Raman peaks from the donor are observed. Thus, the ν_1, ν_2 and ν_3 peaks in the actual RR spectrum are assigned as Raman lines of the complex, which probably correspond to the ν_6, ν_{17} and ν_5 motions of the "free molecule" of the donor [16]. The frequency shift is now attributed to the complex formation process and to the vibronic coupling due to the risonance.

The most interesting feature is the presence in the RREP curves of the complex of a small relative maxi-

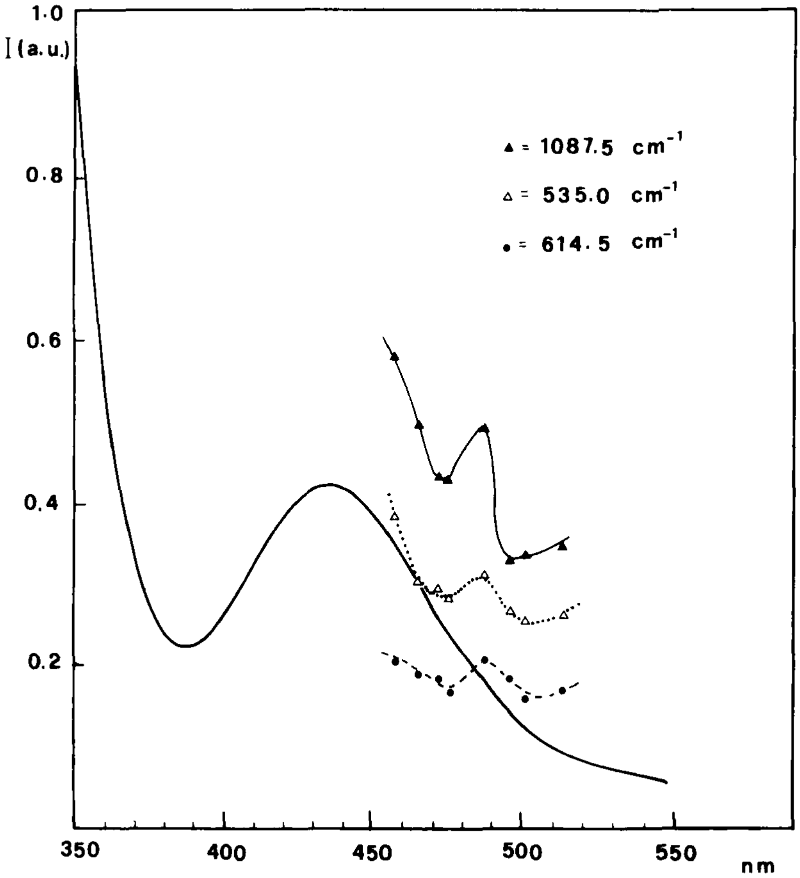

Fig. 2 - Electronic absorption spectrum and RR excitation profiles of $(CH_3)_2SI_2$ in CCl_4

mum at ca. 490 nm, which can be attributed to a fine structure of the profile of the so called "perturbed iodine" electronic transition of these complexes. This maximum falls near a shoulder (ca. 473 nm) of the absorption band and, according to the well known behaviour found in the molecular iodine spectra, is subject in the RR experiments to a red shift from the position of the relevant electronic absorption [8-10].

Such feature reveals the powerful capacity, for the RREP spectroscopy, to bring to light high resolution details, even more than those revealed by the electronic absorption spectra itself (Fig. 2). In fact, the shoulder at ca. 473 nm can be due to a vibrational progression term of the electronic transition of the complex, which appears not well resolved in CCl_4 solution. Vibronic coupling due to the resonance produces in the RREP curves an amplification of the intensity and the red shift determines its separation from the maximum of the profile itself.

Work is now in progress in our laboratory [20], on the nature of these effects and on the theoretical computation of the RREP curves for a large series of stable adducts between organic sulphur compounds and iodine.

Acknowledgements

The authors thank Miss Ronny Kurenta for her contribution in measuring the RR spectra and the Italian Consiglio Nazionale delle Ricerche (Roma) for financial support.

References

1) T.G. Spiro and P. Stein, Ann. Rev. Phys. Chem. 28(1977)501.
2) D.L. Rousseau, J.M. Friedman and P.F. Williams, in Topics in Current Physics, vol. 11 (Springer, Berlin, 1979) p. 203.
3) W. Siebrand and M.Z. Zgierski, in Excited states, vol. 4, ed. E.C. Lim (Academic Press, New York, 1979) p. 1.
4) M.Z. Zgierski and M. Paulikowski, Chem. Phys. 65 (1982) 335.
5) J.A. Shelnutt, J. Chem. Phys., 72 (1980) 3948.
6) S. Sufrà, G. Dellepiane, G. Masetti and G. Zerbi, J. Raman Spectrosc., 6 (1977) 267.
7) L.C. Hoskins, J. Chem. Phys., 74 (1981) 882.

8) S. Matsuzaki and S. Maeda, Chem. Phys. Letters, 28 (1974)27.

9) G.R. Fenstermacher and R.H. Callender Optics Comm., 10 (1974) 181.

10) E. Mulazzi, R. Tubino and G. Dellepiane, Chem. Phys. Letters, 86 (1982) 347

11) E. Mulazzi, R. Tubino and G. Dellepiane, J. of Physique, 42, (1981) 493

12) N.W. Tideswell and J.D. Mc Cullough, J. Am. Chem. Soc., 79 (1957) 1031.

13) M. Good, A. Major, J.N. Chaudhuri and S.P. Mc Glynn, J. Am. Chem. Soc., 83 (1961) 4329.

14) G. Reichenbach, S. Santini and U. Mazzucato, J.C.S. Faraday I, (1973) 143.

15) S. Santini, G. Reichenbach and U. Mazzucato, J.C.S. Perkin II, (1974) 494.

16) "Vibrational spectra of polyatomic molecules", by L.M. Sverdlov, M.A. Kovner, E.P. Krainov, Chp. XII, p. 538, John Wiley, 1974, and references therein.

17) J.P. Perchard, M.T. Forel and M.L. Josein, J. Chim. Phys., 61 (1964) 645.

18) J. Allkins and P. Hendra, Spectrochim. Acta, 22 (1966) 2075.

19) H. Hayashi, J. Chem. Soc. Japan, Pure Chem. Sci., 78 (1957) 101

20) R. Cataliotti, G. Paliani, S. Santini, Work in preparation.

Received: March 16, 1983
Accepted: May 10, 1983