Rotational Resolution in the VUV-Spectrum of CF_3I via Infrared-Ultraviolet Double Resonance Experiments

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This paper reports the double resonance signal observed by combination of a cw CO_2 laser with a pulsed uv ionisation technique (REMPI). The infrared laser was used to pump a single ro-vibrational transition of the ν_1 band of CF_3I, and the resulting change in the two-photon, vuv spectrum was observed. Signals were detected under conditions of mass selectivity using a time of flight mass spectrometer.

Previously unpublished data from infrared-microwave double resonance experiments are also included.

Introduction

The strong 10 μm, ν_1 absorption band (C-F stretch) of trifluoromethyliodide (CF_3I) lies in a convenient spectral region for experiments to be conducted with powerful CO_2 lasers. Infrared-microwave double resonance experiments involving the use of such lasers were reported from this laboratory a number of years ago [1, 2]. The CO_2 laser has the disadvantage that its lines are essentially fixed in frequency, but as result of this the frequency of these lines has been accurately determined [3]. In the double resonance experiments, by measurement of the signals observed in the microwave region, it was possible to identify which infrared transitions of the substance under investigation where coincident with a given CO_2 laser line [4]. This method is particularly effective in the case of a heavy molecule with dense ro-vibrational spectra and in some cases still is the only method to have produced really reliable data (e.g. CF_2Cl_2 [5]). While the method generally makes very reliable rotational assignments based on the observed microwave spectra, there are much fewer data available over the vibrational assignment. In the case of a simple vibration band with associated hot-bands, the vibration assignment usually poses no problem. However, in instances where several bands overlap and worse, in cases where considerable perturbations occur, the data available from the double resonance signals are too limited to be sure which vibrational levels are involved.

An example of such a complex situation is the ν_1 band region of CF_3I. While the double resonance data gave reliable assignments of the rotational J, K, quantum numbers involved, it was clear from the observations [2] that several bands were involved, not simply ν_1. Indeed, further double resonance work showed the situation to be so complex that the data was never published [6]. We use the opportunity of our revived interest in CF_3I to make these data generally available by listing them in Table 1.

Considerable effort has since been devoted to the unravelling of the infrared spectrum of CF_3I, most notably by the groups of Hans Burger and Martin Quack, e.g. [7]. These results have generally confirmed the double resonance rotational assignments and have solved the problems with the vibrational assignments.

In our first double resonance experiments with CF_3I, the very strong signals observed where explained by the 9 μm R(16) line of the normal CO_2 laser pumping hyperfine components of the R(7), $K = 2$ transition of the ν_1 band. The vibrational assignment was made simply on the basis of the intensity of the signals, and fortunately the detailed infrared studies [7] have confirmed that this assignment is indeed correct.

When the problems of carrying out a detailed analysis on the infrared spectrum of CF_3I are considered,

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Table 1. Infrared-microwave double resonance signals (in MHz) with four $C^{18}O_2$ laser lines.

State	J–J′	K	(F–J)	Frequency	DR-effect
9P(12) laser line (1075.0859 cm^{-1}) pumps the $^{Q}R_1(9)$ transition of a hot-band					
lower	8–9	1	19/2	27,366.8	+Abs.
			17/2	27,359.6	+Abs.
			11/2	27,357.1	+Abs.
			15/2	27,352.5	+Abs.
			13/2	27,350.1	+Abs.
lower	9–10	1	21/2	30,405.4	Em
			19/2	30,399.6	Em
upper	9–10	1	21/2	30,282.1	Em
			19/2	30,276.4	Em
			17/2	30,270.8	Em
			15/2	30,268.5	Em
upper	10–11	1	23/2	33,308,9	+Abs.
			21/2	33,304.4	+Abs.
9P(14) laser line (1073.5788 cm^{-1}) pumps the $^{Q}Q_7(11)$ transition of a hot-band					
lower	10–11	7	21/2	33,397.1	+Abs.
			19/2	33,411.6	+Abs.
			25/2	33,502.4	+Abs.
			15/2	33,519.2	+Abs.
lower	11–12	7	19/2	36,492.5	−Abs.
			27/2	36,531.5	−Abs.
			17/2	36,542.5	−Abs.
upper	10–11	7	23/2	33,334.3	Em
			19/2	33,323.8	Em
			21/2	33,308.6	Em
			17/2	33,367.2	Em
upper	11–12	7	23/2	36,353.3	+Abs.
			21/2	36,363.0	+Abs.
			25/2	36,374.0	+Abs.
			19/2	36,395.7	+Abs.
9P(16) laser line (1072.0525 cm^{-1}) pumps the $^{Q}R_5(7)$ transition of a hot-band					
lower	6–7	5	15/2	21,219.6	+Abs.
			11/2	21,235.2	+Abs.
lower	7–8	5	17/2	24,288.2	Em
upper	7–8	5	17/2	24,212.1	Em
upper	8–9	5	19/2	27,260.1	+Abs.
			15/2	27,252.8	+Abs.
9P(14) laser line (1073.5788 cm^{-1}) pumps the $^{Q}P_1(11)$ transition of a fundamental					
ground	10–11	1	17/2	33,504.1	+Abs.
			19/2	33,506.4	+Abs.
ground	11–12	1	25/2	36,561.1	Em
upper	9–10	1	15/2	30,355.8	Em
			17/2	30,357.6	Em
			21/2	30,369.1	Em
upper	10–11	1	17/2	33,393.3	+Abs.
			19/2	33,392.2	+Abs.
			21/2	33,400.2	+Abs.
			23/2	22,404.7	+Abs.

Notation as in [2], the assignment of vibrational states is uncertain (see text).
Measurements were made with an external microwave Stark cell, the assignment as "upper" or "lower" vibrational state is based on the intensity of the microwave signal in the absence of laser radiation.

it is obvious that the situation involved with the analysis of the uv band will probably be even more complex. In this paper we report the results of infrared-ultraviolet double resonance experiments carried out on CF_3I using the coincidence with the 9 R (16) line of the CO_2 laser. This type of experiment ultimately transfers the information from the microwave measurements into the vuv spectral region where the allocation of rotational quantum numbers to particular features is at best uncertain.

Two band systems of CF_3I were measured by Sutcliffe and Walsh [8] in the 110 to 180 nm region using conventional techniques. The 174 nm, $\tilde{C} \rightarrow \tilde{X}$ band system of CF_3I has been more recently studied using REMPI (resonance enhanced multiphoton ionisation) techniques by van den Hoek et al. [9]. These authors carried out spectroscopy on a supersonic expansion jet of CF_3I in an apparatus fitted with a time of flight (TOF) mass spectrometer using a frequency doubled, pulsed dye laser. Since a resonant two-photon process gave rise to the observed spectrum [$a(2+1)$ ionization process], the signals were observed in the 350 nm region.

The experiments described in this paper were carried out in an apparatus similar to that used by van den Hoek et al. [9] with the addition that power from a cw CO_2 laser was also focussed onto the gas jet. Our previous experiments on $^{15}NH_3$ have already demonstrated that this combination can produce observable signals [10, 11]. In the case of CF_3I the spectra involved are much more dense than those encountered with ammonia. The combination of a cw infrared laser with the pulsed laser REMPI/TOF system certainly produces a poor "duty-cycle" for the experiment and, as will be discussed later, this places high requirements on the power of the infrared laser to be used in a successful experiment. However, since the aim of these experiments is to demonstrate rotational resolution in the vuv-region via double resonance experiments, only cw sources have sufficiently narrow line widths for this to be achieved with heavy molecular structures. The CO_2 laser has a line width <1 MHz and consequently pumps selectively a *single* ro-vibrational transition; the double resonance signals observed in the vuv-region are therefore automatically rotationally resolved. In this particular case, by carrying out the double resonance experiment one ultimately transfers the information gained into the microwave region, where extremely high resolution is available via the infrared up into the vuv-region.

Experimental

The REMPI/TOF apparatus consisted of a single vaccum chamber (ca. 50-liter volume) with the 50-cm long, drift tube of a linear TOF mass spectrometer aligned at right angles to the axis of the free expansion jet. The chamber and the TOF were connected over an opening 5 mm in diameter. Pressures in the region of 10^{-3} mbar were maintained in the main chamber using a 700 liter/s diffusion pump, whereas the mass spectrometer was kept at 10^{-6} to 10^{-7} mbar with the aid of a 300 liter/s turbo-molecular pump. Gas was admitted over a pulsed nozzle (General Valve) with a 0.5-mm orifice. Measurements where carried out using a 3% mixture of CF_3I in argon at a stagnation pressure of 3 bar.

Ultraviolet radiation was produced by doubling the output of a Nd:YAG pumped dye laser (Lumonics HY-1200, HD-300) in a KDP crystal (Lumonics Hypertrack). Pulse energies in the range 5 to 50 mJ with pulse lengths of the order of 5 ns with a nominal line width of approximately 0.12 cm^{-1} were produced in the 340-nm region.

Frequency calibration of all the spectra reported in this paper was carried out by simultaneously recording the visible absorption spectrum of iodine [12]. In this way an estimated absolute accuracy of approximately ± 0.02 cm^{-1} was achieved in the 145-nm region.

The cw CO_2-laser was of conventional design and operated in a semi-sealed-off mode. It produced up to 1.5 Watts in the 9.4 μm R-branch region of normal CO_2 with a nominal line width of >1 MHz.

Observations and Discussion

Spectroscopy was carried out on a 3% seeded jet of CF_3I in argon with stagnation pressure of 3 bar. The (2+1) REMPI spectrum observed from the CF_3I^+ mass peak under these conditions in the region 345 to 360 nm is shown in Figure 1. The main features were identified using the data available [8, 9] as shown in this figure. The effective vibration temperature of the CF_3I in the jet was estimated from relative intensities under these conditions to be 60 K.

In the double resonance experiments, the signals arise from a single ro-vibrational level, and in order to predict where signals are to be expected, the selection rules involved must be considered. The vibrational levels involved are shown in Figure 2. Since the infrared laser pumps a ν_1 transition, only the vibronic bands involving this mode are of interest. In principle a transition in the $\mathbf{1}_1^0$, $\mathbf{1}_1^1$, and $\mathbf{1}_1^2$ vibronic bands should be observable. The 9 R (16) CO_2 laser line populates the $J=8$, $K=2$ level of the ν_1 rotational level (1), and the selection rules for the ensuing two-photon transition to the C-state is determined by the overall

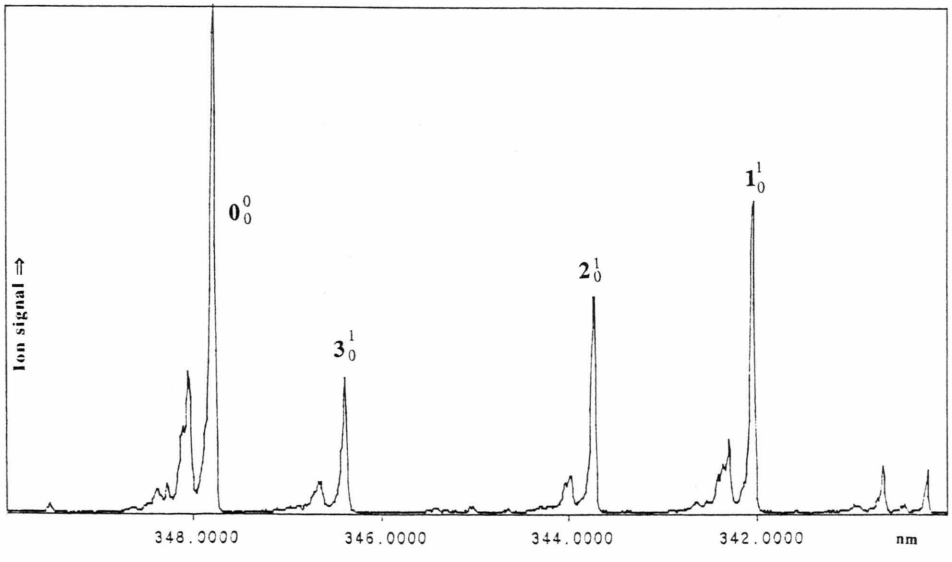

Fig. 1. The two-photon REMPI spectrum of a sample of 3% CF_3I in Argon in the region of 350 nm to 344 nm (single photon wavelengths). Vibrational assignments are shown in the figure. The effective vibrational temperature is calculated to be 60 K under these circumstances.

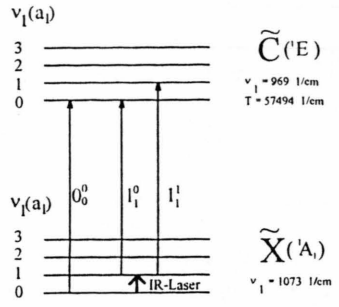

Fig. 2. Schematic diagram of the levels involved in the double resonance experiments.

symmetries. The basic information is given in Figure 2. The transitions involved are $A_1 \mapsto E$ or $A_2 \to E$. In this case only the second-rank of the polarisation tensor makes a contribution [13], and the overall selection rules for the two-photon transitions are $\Delta J = 0, \pm 1, \pm 2$ and $\Delta K = \pm 2$.

Precise information is available only over the ground electronic state of CF_3I [1, 7]. However, combination with the information over the C-state enables one to predict the wavelength regions in which a double resonance signal would be expected to be observed. These regions correspond to laser wavelengths of 354.4 nm, 348.5 nm and 342.8 nm for the $\mathbf{1}_1^0$, $\mathbf{1}_1^1$, and $\mathbf{1}_1^2$ vibronic bands, respectively.

The most reliable prediction could be made for the $\mathbf{1}_1^0$ band since this did not require knowledge of the rotational parameters in the upper state. The signal observed in the region of 354.4 nm when 1.3 Watts of CO_2 radiation was introduced into the chamber is shown in Figure 3. As can be seen from this figure, the signal observed appeared as a close doublet. The signal was centered at 354.422 nm, and the separation between the two peaks was 2.25 cm^{-1}. The signal approximately a factor of 100 down on the REMPI signals shown in Figure 1. Even if the infrared laser is saturating the ground state transition, a reduction in intensity would be expected since the signal arises from only a single ro-vibronic transition. This particular case was fortuitous since in the absence of infrared radiation no other signals were present, so that there was little difficulty in identifying the double resonance signal.

This was not the case with the signals expected for the other two vibronic bands $\mathbf{1}_1^1$ and $\mathbf{1}_1^2$. The $\mathbf{1}_1^1$ band lies very close to the strong $\mathbf{0}_0^0$ band, and the $\mathbf{1}_1^2$, band lies in the region of the almost equally intense $\mathbf{1}_0^1$ band. In both these cases the problem of detecting a relatively weak double resonance signal in the presence of other much stronger signals proved to be too much, and no double resonance signal was positively identified.

The doublet structure of the double resonance signal shown in Fig. 3 can be explained as transitions

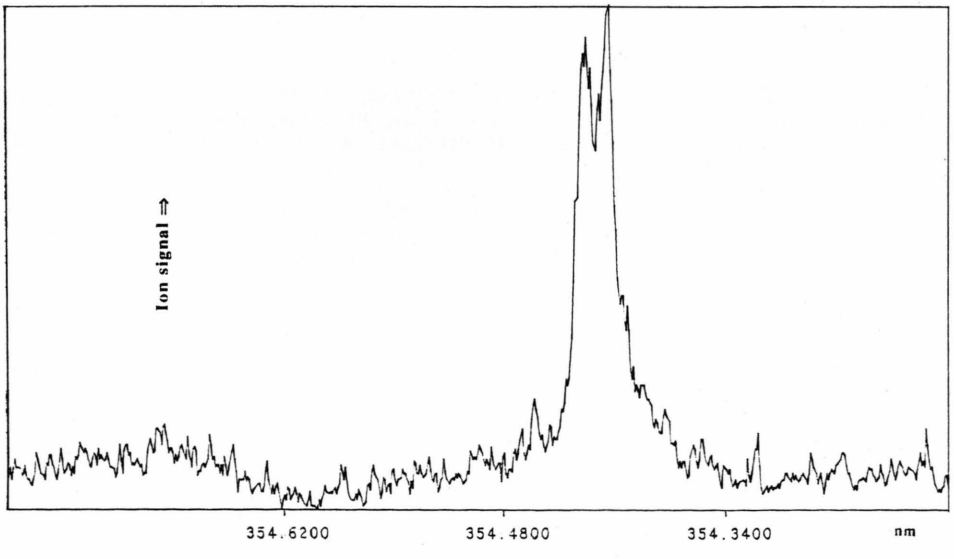

Fig. 3. Double resonance signal observed at 354.422 nm. The separation between the two components of the doublet structure is 2.25 cm^{-1}.

from the X, $v_1=1$, $J=8$, $K=2$ level to the $K=0$ and $K=4$, $v_1=0$ levels of the $\tilde{C}$-state. The B rotational constant of CF_3I is of the order of $0.05\,cm^{-1}$, the J structure could therefore not be resolved. Since the two transitions giving rise to this signal start from the same ground state level, the separation between the two components is the energy difference between the $K=4$ and the $K=0$ levels of the $v=0$ level of the $\tilde{C}$ state. Thus the measured separation of $2.25\,cm^{-1}$ is equal to approximately $16(A-B)$, which yields $(A-B)=0.14\,cm^{-1}$ in the $\tilde{C}$ state. This result seems quite reasonable since in the ground state $(A-B)=0.14129$ [7].

From this single double resonance signal alone, unfortunately, no further parameters of the $\tilde{C}$ state can be determined. The observation does, however, confirm the basic reliability of the parameters available [8, 9].

Conclusions

These results confirm the potential usefulness of this type of experiment for extending the high resolution and assignment certainty which is available from spectroscopy at longer wavelengths into the vuv-region. The experiments were performed on a cold supersonic jet under conditions of mass selectivity. Although under the present circumstances, since we were using a pure sample, the mas selectivity was largely irrelevant, these results illustrate the potential of the method for dealing with samples of a more complex nature. Probably the most important field of application involves situations in which samples of varying mass are to be studied, such as is the case with the production of clusters.

To realize its maximum potential, this method should be carried out using a tunable, narrow band infrared source, which would allow at least Doppler-limited resolution of the infrared spectrum to be achieved. We have attempted to observe double resonance signals using tunable diode lasers as the infrared source, but these experiments have failed to produce positive results. So far, we have only been successful in producing double resonance signals in CF_3I, $^{15}NH_3$ [11, 12] and $^{14}NH_3$ [14] using CO_2 lasers. These experiments have shown that a minimum of approximately 300 mW infrared radiation was required to detect the double resonance signals. Such requirements are well outside the specifications of the diode laser available at present in the mid-infrared region. Indeed, the simultaneous requirements on wide tunability, narrow line width, and high output power are far beyond the capabilities of any device so far available.

Acknowledgements

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