Laser Ionisation Spectroscopy of Formyl Fluoride

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A vibronic band of formyl fluoride near 39,511 cm^{-1} has been observed using multiphoton ionisation spectroscopy. From the analysis of the partially resolved rotational structure, the rotational parameters of the (0, 2, 0, 0, 0, 0) vibrational level of an electronic state near 39,000 cm^{-1} have been determined: $A = 92.50\,(1.46)$ GHz and $(B + C)/2 = 11.23\,(30)$ GHz. The term value was determined to be 39,510.93 (30) cm^{-1}.

Introduction

Most spectroscopic investigations of the small asymmetric-rotor molecule formyl fluoride (HCOF) have concentrated on its infrared and microwave spectra [1–3]. The only information on the ultraviolet spectrum appears to be limited to the work of Giddings and Innes [4], which was carried out under conditions of medium resolution.

Formyl fluoride exhibits a very strong absorption band in the 10 μm region, which is composed of ν_3 and ν_6 in HCOF and of only ν_3 in DCOF. A number of investigations involving the use of CO_2 lasers, which make use of this strong absorption, have been reported from this laboratory: Intense FIR laser oscillation was produced via pumping with CO_2 lasers [5, 6] and infrared-microwave double resonance was successfully applied to DCOF to obtain values for the major parameters of a number of vibrationally excited states [7]. This latter work is one of a few examples of this technique being employed to determine band parameters directly. Many double resonance signals have also been observed in HCOF [8], but analysis has so far been hindered by the effects of Coriolis coupling between ν_3 and ν_6 [2]. Recently, the high resolution FTIR spectrum of five fundamentals of HCOF has been published [9]. In the present work an analysis of the effects of Coriolis coupling between ν_3 and ν_6 has been carried out.

The strength of the IR-MW double resonance method is that it establishes definite links between infrared frequencies and individual pure rotational transitions. The extension of this technique to complex electronic spectra has obvious advantages, and we have demonstrated that one can successfully combine cw CO_2 lasers with pulsed uv lasers to carry out such experiments [10–12]. Since our previous double resonance work on HCOF [8] has identified a number of ro-vibrational transitions which coincide with definite CO_2 laser lines, this makes HCOF a candidate for an extension of the UV-IR double resonance investigations.

The technique so far employed involved the combination of resonance enhanced multiphoton ionisation spectroscopy (REMPI-spectroscopy) with the infrared laser radiation. Since there was no detailed information available on the uv spectrum of HCOF, we decided to attempt to measure a REMPI spectrum.

In its ground state, formyl fluoride is a near prolate rotor with $A = 3.04065\ \mathrm{cm}^{-1}$, $B = 0.39228\ \mathrm{cm}^{-1}$ and $C \cong 0.34679\ \mathrm{cm}^{-1}$ [1]. In the work of Giddings and Innes [4] a large number of vibrational bands was identified in the region 200 to 270 nm, which appeared to arise from two electronic states. Resolution of some rotational structure was achieved in a few bands, and this resulted in rough values of $A = 2.16\ \mathrm{cm}^{-1}$ and $(B + C)/2 = 0.36\ \mathrm{cm}^{-1}$ for a few vibronic levels being determined.

One problem with observing ionisation spectra is that the ionisation potential of HCOF appears not to have been measured. Comparison with similar molecules indicates that it probably lies considerably above 10 eV. Thus it would appear that, if any of the vibronic levels already investigated [4] was to be used as intermediate resonant level, a total of three photons would be required to produce ionisation. Two schemes are possible in this case; a single photon absorption followed by a two-photon ionisation set (a [1 + 2] REMPI-process), or the first step followed by a second resonant step to a state slightly below the

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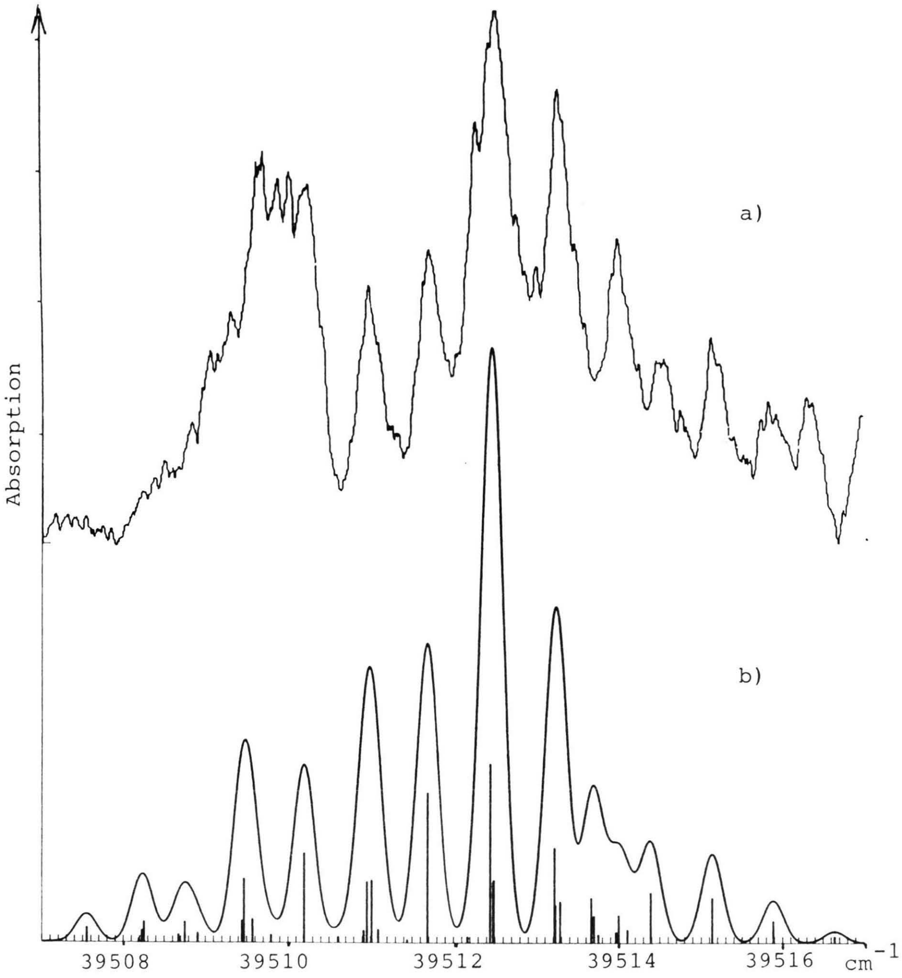

Fig. 1. a) The spectrum observed in the region 39,507 to 39,517 cm^{-1}. b) The simulated spectrum produced using the parameters of Table 1, an effective rotational temperature of 2.0 K, and an effective line width of 0.15 cm^{-1} with the program *BC*2. The band appears to be an *a*/*b*-hybride, and the best reproduction of the spectrum in a) was achieved with a ratio of *a*-type to *b*-type of 3 to 1.

ionisation threshold and then by a third step into the ionisation continuum (a [1 + 1 + 1] REMPI-process). The latter process would certainly be the most efficient process, but in the case of single color measurements being carried out, it naturally places more stringent requirements on the energy level scheme present in the molecule under investigation. Consequently, this type of process would be expected to occur relatively infrequently.

Experimental

The REMPI/TOF apparatus consisted of a single vacuum 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 a 5-mm opening. 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.

Formyl fluoride was prepared by formic acid as described by Nesmeyanov and Kahn [13] and the product collected at 77 K. For the REMPI measurements, a sample of the gas was condensed into a passified steel pressure bottle and then pressurized with argon so that a roughly 3% mixture at a stagnation pressure of 3 bar was produced. The gas mixture was admitted at this pressure to the vacuum chamber through a pulsed nozzle (General Valve) with a 0.5-mm orifice. Despite all passification precautions, the formyl fluoride sample deteriorated fairly quickly under these conditions, and the pressure vessel had to be refilled daily.

Tunable ultraviolet radiation in the 270 to 230 nm region was produced by pumping a Lumonics HD-300 dye laser with the third harmonic of a Lumonics HY-1200 Nd:YAG laser and then doubling the output in a BBO crystal (Lumonics Hypertrack). Pulse energies in the region of 10 mJ with pulse lengths of the order of 5 ns and a nominal line-width of approximately 0.12 cm^{-1} were produced.

Frequency calibration of all the spectra reported in this paper was carried out using a Burleigh WA 4500 wavemeter.

Observations

The operation range of the laser system allowed us to investigate a spectral region in which Giddings and Innes [4] reported a considerable number of vibration bands. However, REMPI signals were only observed in one small region centered at 39,512 cm^{-1}. The spectrum observed with the TOF spectrometer tuned to a mass peak of 48 (HCOF) is shown in Figure 1. The observed spectrum (Fig. 1a) extended over roughly 10 cm^{-1} and appears to exhibit partially resolved rotational structure. The high frequency side of the spectrum displays a fairly regular structure with spacings of approximately 0.7 cm^{-1}. This spacing suggests that one is dealing with a predominantly *a*-type spectrum. Under these circumstances, regular structures with a spacing of roughly $(B + C)$ would be expected, which in this case should be in the region of 0.7 cm^{-1}.

The band involved appears to be that measured at 39,512 cm^{-1} by Giddings and Innes [4] and assigned by them as involving a transition between $v = 0$ of the ground electronic state to a vibrational level of an upper state with $(v_1, v_2, v_3, v_4, v_5, v_6) = (0, 2, 0, 0, 0, 0)$, i.e. an upper state in which only the $C=O$ stretching motion is doubly excited. No rotational structure was reported for this band.

Analysis and Discussion

The spectrum shown in Fig. 1a appears to be best described as a predominantly *a*-type band with its origin near 39,511 cm^{-1}. The regular features on the high frequency side of the origin then appear to be the R-branch of an *a*-type spectrum. Assuming this to be the case, attempts were made to reproduce the observed spectrum by a combination of a least squares fit of the main spectral features and generation of the band contours.

Table 1. Molecular Parameters of Formyl Fluoride.

	Ground State[a]	Upper State[b]
A	91.156513 GHz	92.5 (14) GHz
B	11.7691507 GHz	11.23 (30) GHz*
C	10.3967610 GHz	
Term	0	39,510.9 (3) cm^{-1}

* This parameter is $(B + C)/2$; the band contour suggested a value of $(B - C) \cong 0.4$ GHz.

[a] From [1]; the distortion parameters given in [1] were assumed for both levels.

[b] The (0, 2, 0, 0, 0, 0) vibrational level of an electronic state near 39,000 cm^{-1}.

As can be seen from Fig. 1b, we were able reproduce the high frequency side of the spectrum adequately using rotational constants quite similar to those of the ground state (Table 1), an effective line width of 0.15 cm^{-1}, and an effective rotational temperature of 2 K. The main problem lies with the P-branch region, i.e. the features to the low frequency side of 39,511 cm^{-1}. The calculated spectrum (Fig. 1b) indicates two strong P-branch signals which coincide with the broad feature near 39,510 cm^{-1}. In the experimental spectrum, however, there appear to be additional signals in this region which arise from some source other than the band under consideration.

As mentioned in the introduction, the ionisation potential of formyl fluoride is almost certainly considerably higher than 10 eV. Thus, when operating at 39,500 cm^{-1}, one probably needs a third photon to achieve ionisation. This would probably mean that for efficient ionisation to take place, a second intermediate level (i.e. a [1 + 1 + 1] process) would be necessary. This requirement obviously reduces the probability that the required conditions will be fulfilled by a particular set of levels and probably explains why we were not able to observe an ionisation signal with most of the bands reported by Giddings and Innes [4].

Assuming this to be the case, the itensities of the spectrum shown in Fig. 1 are almost certainly influenced by the properties of this second level. Only in the case of the second intermediate level being completely diffuse and very broad, could one expect to obtain a faithful reproduction of the spectrum arising from the first resonant level. Thus it would appear possible that the deterioration of resolution below

39,512 cm^{-1} is due to the properties of the second intermediate (unknown) level rather than those of the (0, 2, 0, 0, 0, 0) level.

As can be seen from the results given in Table 1, the rotational parameters of formyl fluoride in the (0, 2, 0, 0, 0, 0) vibrational level of this electronic state near 39,000 cm^{-1} appear to have changed only slightly from those of the ground state [1]. We were unfortunately not able to resolve any asymmetry doubling in the spectrum observed (Fig. 1), and consequently were not able to determine the value of $(B - C)$ directly. The contour analysis suggested that this splitting was very small, with $(B - C)$ of the order of 0.4 GHz, making formyl fluoride very close to being a symmetric rotor in the excited state.

It is well known that the determination of the A rotational parameter from an a-type spectrum is difficult, and the value we obtained (Table 1) is probably less accurate than the standard deviation of our fit would lead one to believe. The value given in Table 1, when converted to wavenumbers is, $A = 3.08\ \text{cm}^{-1}$. This differs considerably from that reported by Giddings and Innes [4]. The low resolution available in this early work [4], resulted in rotational structure being observed only when a band was predominantly b-type in character, i.e. the spacing in the rotational structure is mainly dependent on the large A rotational constant. For a (0, 1, 0, 0, 1, 2) level at 39,192.12 cm^{-1}, rotational constants of $A = 2.162\ \text{cm}^{-1}$ and $(B + C)/2 = 0.361\ \text{cm}^{-1}$ were reported [4]. The level we have investigated here is energetically very close to that analysed by Giddings and Innes [4] and differs mainly in that the low frequency modes are excited in the latter and not the former. Therefore, it is rather unusual that we arrive at such largely different values for the A rotational parameter. As already mentioned, our value is not particularly accurate, but in would seem unlikely that this could account for such a large difference, 2.1 cm^{-1} compared to almost 3.1 cm^{-1}. Indeed, at the beginning of this work we attempted to reproduce the spectrum of Fig. 1 with the A parameter fixed in the region of 2 cm^{-1}, with no success. The best results were obtained only when the A rotational parameter was allowed to approach its ground state value. At present we have no explanation for this apparent discrepancy.

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