PHOTOLYSIS OF MOLECULES BY AN INFRARED HIGH-POWER LASER PULSE

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Received 4 July 1975

We report the spectra of visible luminescence which accompanies the infrared photolysis of molecules by an intense CO_2 laser pulse. The molecules studied were C_2H_4 , C_2F_3Cl , CH_3OH , CH_3NO_2 , CH_3CN , CF_2Cl_2 and BCl₃. A gated system recorded the signal during the first 100–200 ns after the laser pulse, i.e., during the collisionless dissociation phase. The dissociated products were identified. The mechanism of the infrared photolyses is discussed and compared with UV photolyses.

1. Introduction

In our previous paper [1] we investigated the kinetics of visible luminescence in BCl₃ which occurs when the molecules resonantly absorb intense infrared radiation. It was shown that the molecules can dissociate instantaneously due to the build-up of stored vibrational energy in the absorbing molecules, and that this process requires no collisions. Thus the dissociation of the molecules is a result of a primary photochemical process because the molecules dissociate in a time shorter than that between two successive collisions. Later in ref. [2] it was shown that this type of dissociation in an intense infrared field is a highly selective process. This was demonstrated by achieving isotope selective reactions of dissociated molecules. An enormous enrichment factor was achieved later in the separation of sulphur isotopes by means of the selective dissociation of SF_6 molecules by intense CO_2 laser radiation [3].

In general, the mechanism of dissociation of molecules in an infrared field may differ from the dissociation by high-energy photons. The present work gives some evidence of this through the investigation of the fluorescence spectra of excited radicals formed in the instantaneous collisionless phase of dissociation of a number of molecules by the strong infrared field of a CO_2 laser. The molecules under study have absorptions in the 9 to 10 micron region. They are: C_2H_4 , CH_3OH , CH_3CN , CH_3NO_2 , C_2F_3CI , CF_2CI_2 . We emphasise that at the present time we have not detected the radicals formed in the ground state, but only in excited electronic states.

2. Experimental

The source of the high-intensity IR field was a TEA CO_2 tunable laser which produced 1.5 J 100 ns pulses at the repetition rate of 3 s^{-1} . The power density in the focal region was about 10⁹ W/cm². The laser radiation was focused into a gas cell and the luminescence was detected through a side window. The detection system included the monochromator MDR-2, a photomultiplier, a gated box-car integrator and a chart-recorder. The gate was 150 ns, synchronous with the laser pulse and the luminescence within this time interval corresponded mainly with the collisionless dissociation of molecules. This eliminated the detection of spectra of the radicals formed in the secondary processes, i.e., the radicals formed in chemical reactions after the dissociations. The spectra were recorded at first with the minimum possible gas pressure in the cell, which was usually less than 1.0 torr with a resolution of about 20 Å. The spectra were taken at a higher resolution (2 Å) at elevated pressures for the final identification of the observed bands. The identification of the spectra was facilitated by using refs. [4-6].

The gases used for C_2F_3Cl and CF_2Cl_2 were technically pure, BCl_3 was 98% pure (2% HCl). The remainder

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Fig. 1. A part of the luminescence spectrum of dissociated products from C_2F_3Cl . Pressure of C_2F_3Cl 2 torr, resolution 20 Å.

were chemically pure. All gases were additionally purified by trap-to-trap distillation before use. In some cases, for example with CH_3OH , the gas flowed through the cell at a rate which provided a complete change of the gas in the cell between two successive pulses.

3. Results

3.1. C_2F_3Cl molecules

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The visible luminescence spectrum (fig. 1) was observed at pressures down to 1 torr and is represented only by narrow bands which were identified as the Swan bands of the C_2^* molecule $(d^3 \Pi_g \rightarrow a^3 \Pi_u$ transition). The unresolved maximum centered near 4000 Å is attributed to the luminescence of carbon particles in an intense laser field. No other excited radicals such as CCl^{*} or CF^{*} were detected even at higher pressures.

3.2. C_2H_A molecule

The luminescence spectrum of this molecule was also obtained at a pressure of about 1 torr and was practically identical with that of C_2F_3Cl .

3.3. CH₃OH molecule

The luminescence spectrum was taken at a pressure of 1.2 torr with a fast gas flow system. A large number of bands were recorded in the visible and UV regions. Fig. 2 represents the luminescence spectrum. Certain bands were identified as belonging to the CH^{*}, OH^{*} and C₂^{*} radicals whereas several others have not been identified. Their centres lie at 2445, 2500, 2560, 2595, 2735, 3650, 3685, 4145, 4210 and 4175 Å. One re-



Fig. 2. A part of the luminescence spectrum of dissociation products from CH₃OH. CH₃OH pressure 1.2 torr, resolution 20 Å. The C-O bond is excited ($\nu = 1034 \text{ cm}^{-1}$). The fine structure of the luminescence bands is encircled at a resolution of 5 Å, pressure 10 torr.

markable and very curious result is that in the collisionless dissociation phase the C_2^* bands are clearly seen. It should be noted that the above-mentioned results for boron and sulphur isotope separation through the dissociation of BCl₃ and SF₆ molecules indicate the extreme selectivity of such a dissociation process, and so it is difficult to hold that the luminescence of C_2^* arises from the dissociation of impurities in CH₃OH.

3.4. CH₃CN molecule

The radical luminescence is observed at pressures somewhat higher than 1 torr and consists mainly of well resolved bands which belong to CN^* and C_2^* radicals (the intensity of C_2^* radicals in this case is low). The band centered at 3280 Å has not been identified.

3.5. CH₃NO₂ molecule

The minimum pressure, at which it was possible to record the luminescence spectrum of dissociated products in CH_3NO_2 , was about 5–6 torr, although the most intense bands of CN^* were observed at 1 torr. The luminescence spectrum can be obtained from the dissociation of the molecules by pumping them through various bands (table 1) at 9.2 and 10.7 μ . The radicals formed in these two cases are the same, i.e., CH^* , CN^* , C_2^* (very faint), OH^* and O_2^* or NH^* (fig. 3). But there is a substantial difference in band intensities and in the distribution of intensity between the lines within the band – the luminescence of OH^* and NH^* or O_2^* bands is 1.5-2 times more intense when dissociated through

Table 1

A comparison of dissociation products in vacuum UV photolyses with IR photolyses

Molecules	Vibration frequency excited by CO ₂ laser (cm ⁻¹)		Products			
			IR photolysis		UV photolysis [7]	
C ₂ F ₃ Cl	ν ₄ = 1058		C [*] _2		-	•
C ₂ H ₄	$\nu_7 = 949.3$	•	C ₂ *		CH₂C + H₂ HC≡CH	(1)
					СH₂С +́ н + н СН₂СН + Н	
СН₃ОН	$\nu_{\rm g}$ = 1034		CH [*] OH [*]		$CH_2O + H_2$ $CH_3O^* + H$	(1) (2)
			C ₂ unidentified p	roducts	CH₃÷OH [*]	(3)
CH₃CN	ν ₄ = 918		CN [*] C [*] CH [*]		$H + H_2CCN$ $CH_3 + CN^*$	(1) (2)
CH3NO2	a) $v_7 = 921$ b) $v_{13} = 1097$		CN^* CH^* OH^* $NH \text{ or } O_*^*$		CH ₃ + NO ₂ CH ₂ O + NOH	(1) (2)
CF2Cl2 BCl3	$ \nu_6 = 922 $ $ \nu_3 = 956 $	·	CCI [*] BCI [*] unidentified p	roducts	-	



Fig. 3. A part of the luminescence spectrum of dissociation products from CH₃NO₂. Gas pressure 10 torr, resolution 20 A. Solid line: the deformation vibration α (HCH) and β (NCH), $\nu_{13} = 1097 \text{ cm}^{-1}$ is excited. Dotted line: the C–N and deformation vibration γ (ONO), $\nu_7 = 921 \text{ cm}^{-1}$ is excited. The structure of the 3880 Å band is shown with a resolution of 2.5 Å at a CH₃NO₂ pressure of 17 torr. The structure of the band is characteristic of the CN radical. excitation of the ν_{13} vibrational mode compared to that when we excite the ν_7 mode.

3.6. CF₂Cl₂ molecule

In this molecule luminescence can be observed only at high pressures (≈ 10 torr). The CCl^{*} radical can be identified from the spectrum.

3.7. BCl₃ molecule

As previously discussed [1], the spectrum for this molecule in the range 4300-6000 Å is continuous at a resolution of 15 Å, and its source has not been identified. In the UV region we have observed BCl radical bands ($A^{1}\Pi \rightarrow X^{1}\Sigma^{+}$ transition). But the appearance of this luminescence is time delayed after the laser pulse, and it is believed that it results from secondary processes, probably by reactions between dissociation products and BCl₃, rather than by non-collisional molecular dissociation.

4. Discussion

The results stated show that the process of non-collisional molecular dissociation in a strong IR field is rather common, since this effect has been observed in various polyatomic molecules differing in both structure and composition. The data obtained make it possible to draw some conclusions on the dissociation mechanism.

Table 1 shows that molecular dissociation occurs via different channels at the same time and necessitates the simultaneous fission of several different bonds. In this case it is of no importance which of the bonds is excited initially by the IR field. This is probably caused by the excitation of many molecular vibrations due to noncollisional intramolecular relaxation of the molecules directly excited by the strong IR field to high vibrational levels of a mode which absorbs laser radiation. It follows from our experimental results that a molecule accumulates energy in excess of the dissociation energy in a time shorter than 10^{-7} s. We propose therefore that the molecule accumulates a considerable energy and then breaks up. We should point out that some decay mechanisms, say, $C_2H_4 \rightarrow C_2^* + \dots$, demand that a molecule be dissociated practically to separate atoms. Only/the most stable bonds (C=C) are preserved.

If we compare the products of molecular dissociation during high-energy photon photolysis (table 1) and IR photolysis we can see that they are completely different, to judge at least by excited products; furthermore, during the usual photolysis under long excitation pulse conditions radicals may result from secondary processes as well. Specifically, during IR photolysis no excited radicals which contain more than two atoms have been observed anywhere.

In the case of CH₃CN the resulting spectrum can be fully identified. This was observed during short time intervals following directly after the excitation pulse maximum, that is under collisionless conditions, and also the spectrum of the so-called "delayed" luminescence stage when collisions between highly excited molecules initiate their dissociation. This points to the fact, that the paths of molecular dissociation during IR photolysis are conditioned not by the presence of a strong field but by the very mechanism of energy accumulation by molecules, regardless of whether they derive this energy from the field or when colliding with other molecules. Of course, this holds only when

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there is an excess over a certain "threshold" level of molecular excitation by a strong field.

The results given enable us to conclude that it is impossible to break selectively particular chemical bonds of a molecule in a strong IR field. However, the differentiation of relatively different (excited and unexcited) molecules is practicable. As can be seen from previous work [2], such selectivity exists even in those cases with the same molecules but of different isotopic composition.

One of the basic questions is whether the radicals observed are initial products of dissociation or if they are associated with secondary reactions of the radicalradical and radical-molecule type. So far, there is no simple answer to this problem. For instance, the formation of C_2^* radicals in the case of CH₃OH and CH₃NO₂ might be related to secondary reactions. However, C_2^* radicals are formed in a time of $\approx 10^{-7}$ s, even at a pressure much less than 1 torr, that is, reactions occur in a shorter time than that of one gas-kinetic collision. This is feasible only when the velocity of the dissociated particles is much higher than the mean thermal velocity of the surrounding molecules or if the molecules were associated in the ground state (dimers).

For further studies of the mechanism and characteristics of collisionless molecular dissociation in a strong IR field it is necessary that dissociation products should be investigated by other methods, among which is laser excitation of fluorescence of the radicals arising from the main state.

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