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INFRARED LASER MULTIPLE PHOTON CHEMISTRY OF NITRO-METHANE

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Summary

The CO_2 laser-induced dissociation of nitromethane (CH_3NO_2) is investigated through luminescence and laser-induced fluorescence studies. The main reaction channel is found to involve fission of the C–N bond. Both ground state and electronically excited NO_2 molecules are produced. Emission from electronically excited diatomic fragments is also observed. Interestingly, at pressures below 0.5 Torr the $CN^*(B^2\Sigma^+)$ radical is produced unimolecularly. The mechanism of the fragmentation is discussed.

1. Introduction

Infrared laser multiple-photon-induced chemistry (IRMPC) provides an excellent way of studying unimolecular chemical reactions, a fact which is often overshadowed by the possible technological applications to isotope separation [1]. IR activation with short laser pulses can result in a clean dissociation which is free from heterogeneous effects.

An aspect of IRMPC which is of particular interest involves the possibility of vibrational excitation well above the lowest energy reaction channel, followed by reaction from higher lying channels. This process could be more important under the fast laser activation at high power densities than under collisional (thermal) activation [2].

There have been several reports of collisionless production of high energy fragments which, at least superficially (see Section 3), suggest excessive vibrational excitation. In an early study Ambartzumian *et al.* [3] dissociated a number of polyatomic molecules using a focused CO_2 laser beam and detected luminescence from a variety of diatomic photofragments during the first 150 ns after the laser pulse. More recently Campbell *et al.* [4] have reported

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the collisionless production of the C_2 molecule through the CO_2 laser disso-
ciation of C_2H_5CN, C_2H_5OH and $C_2H_5NH_2$. Similarly, the collisionless pro-
duction of C_2 from C_2H_4 has been reported by Hall et al. [5]. Chemical
evidence (in the collisional regime) of approximately 21 kcal mol^{-1} excess
excitation has been presented by Rosenfeld et al. [6] for ethyl vinyl ether.

Nitromethane (CH_3NO_2) was among the molecules investigated in the
early study of Ambartzumian et al. [3]. Upon CO_2 laser excitation of
CH_3NO_2, luminescence from a variety of diatomic molecular fragments was
detected. The luminescence of the different fragments was recorded at pres-
sures of 5 - 6 Torr, although the most intense bands of CN were observed at
1 Torr. Experiments on nitrogen isotope separation have also been reported
in mixtures of $CH_3{}^{14}NO_2$ and $CH_3{}^{15}NO_2$ by Chekalin et al. [7].

In this study we reinvestigate in more detail the IRMPC of CH_3NO_2.
Both the lowest activation energy reaction channel, involving the fission of
the C–N bond to give CH_3 and NO_2, and high activation energy channels, such
as the production of CN radicals, are investigated. Particular emphasis is
placed on the pressure dependence of the laser-induced fluorescence (LIF)
and of the luminescence of the fragments in an effort to understand the
unimolecular or collisional nature of their formation process.

2. Experimental

The IR laser was a Tachisto TEA CO_2 laser (approximately 0.8 J, 0.5 Hz,
200 ns full width at half-maximum and multimode). The IR pulses were
focused into an anodized aluminum reaction cell, equipped with NaCl win-
dows, through a 10 cm focal length BaF_2 lens. The pulse energy was measured
using a Scientech energy meter. The laser utilized for LIF was a Molectron
nitrogen-laser-pumped dye laser.

The emission viewed at 90° to both laser beams was either dispersed by
a 0.5 m Jarrell–Ash monochromator or isolated through filters and detected
using an RCA C31034A GaAs photomultiplier. The transient signal was cap-
tured by a Biomation 610B transient recorder (100 ns channel^{-1}) and aver-
aged with a Tracor-Northern NS-570 digital signal analyzer. The CH_3NO_2
used was Aldrich spectrophotometric grade (Gold Label).

3. Results and discussion

3.1. The lowest activation energy reaction channel
Based on our present knowledge of the IR multiple-photon dissociation
(IRMPD) processes, the lowest activation energy reaction channel should be
heavily favored. The kinetics of the thermal decomposition of CH_3NO_2 has
been the subject of early studies [8, 9]. The activation energy E_a for the
thermal decomposition has been determined [8] to be 53.6 kcal mol^{-1}. Uti-
lizing standard enthalpies of formation the enthalpy ΔH of the reaction

$$CH_3NO_2 \longrightarrow CH_3 + NO_2 \qquad (1)$$

has been calculated [9] to be 52.3 kcal mol^{-1}. The proximity of the values of E_a and ΔH suggests that the initial and rate-determining step in the thermal decomposition of CH_3NO_2 is the fission of the C–N bond according to reaction (1). Subsequent radical reactions lead to a variety of end products.

We dissociated CH_3NO_2 with the TEA CO_2 laser tuned to the P(36) line of the 10.6 μm band; this line is in resonance with the ν_7 mode of CH_3NO_2 (a C–N stretching vibration) [10]. The P(36) line was found opto-acoustically to represent the best compromise between the absorption strength and the output power of the laser, i.e. the opto-acoustic signal was largest for the P(36) line, indicating the maximum energy deposition in the molecule. In order to monitor the occurrence of reaction (1) we utilized the LIF of NO_2. NO_2 was excited by a dye laser at 505 nm and its fluorescence was isolated by the use of a Corning 3-68 filter. Very strong NO_2 fluorescence was observed indicating, as expected, the importance of reaction (1). This main dissociation channel of CH_3NO_2 was not, however, detected by Ambartzumian et al. [3]. The dependence of the NO_2 LIF intensity I_{LIF} on the CH_3NO_2 pressure is shown in Fig. 1. At low pressures (0.08 - 0.5 Torr) the production of ground state NO_2 molecules (which is proportional to I_{LIF}) shows approximately a linear dependence on the CH_3NO_2 pressure ($I_{LIF} \propto P^{0.9}$). At pressures above about 0.5 Torr, however, collisional effects become important.

We also found that a small fraction of the NO_2 molecules resulting from the dissociation of CH_3NO_2 is produced in an electronically excited state. This process was studied by monitoring the NO_2^* luminescence in the absence of dye laser excitation. The variation of the NO_2^* luminescence intensity with CH_3NO_2 pressure is shown in Fig. 2. The behavior is analogous to that observed for ground state NO_2 production. In the low pressure regime (0.03 -
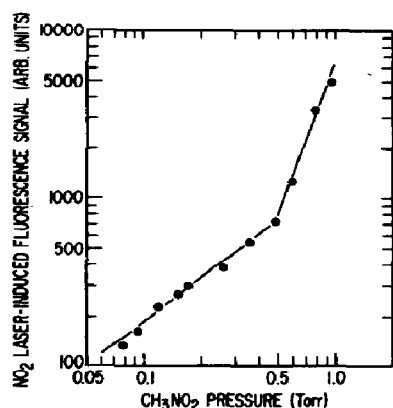

Fig. 1. The pressure dependence of the NO_2 LIF signal. TEA CO_2 laser at 10.76 μm (0.5 J pulse^{-1}) and dye laser at 505 nm.
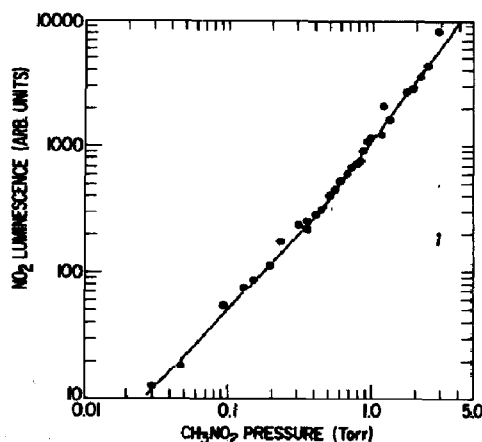
Fig. 2. The pressure dependence of the NO_2 luminescence. TEA CO_2 laser at 10.76 μm (0.5 J pulse^{-1}).

0.5 Torr) a nearly linear ($P^{1.2}$) dependence is found, followed by a collisional regime above about 0.5 Torr.

The linear dependence of the NO_2 LIF signal on CH_3NO_2 pressure at $P < 0.5$ Torr implies that the excited CH_3NO_2 dissociates in a unimolecular fashion to give NO_2 (reaction (1)). A linear pressure dependence for the NO_2^* production below 0.5 Torr suggests that NO_2^* may be the result of a vibrational → electronic (V → E) energy transformation process occurring during the dissociation of vibrationally excited CH_3NO_2. However, $E_a \approx \Delta H$ for reaction (1) [9] and, since the unimolecular reaction rate increases rapidly with excess energy, electronic excitation of NO_2 by a V → E process would require a fast up-pumping rate, resulting in excess vibrationally excited CH_3NO_2. Of course only a small fraction of CH_3NO_2 molecules, corresponding to the high energy tail of the vibrational energy distribution, could give rise to NO_2^*.

The production of NO_2, NO_2^* and also CN^* (see Section 3.2) shows a collisional behavior at $P > 0.5$ Torr. It is unlikely that bimolecular reactions leading to these various products will become established at the same pressure (0.5 Torr). Moreover, it is known [8, 9] that the thermally induced reaction (1) remains unimolecular to pressures as high as 400 Torr. There is no obvious reason why the same reaction induced by the laser should change its molecularity above 0.5 Torr. For these reasons we ascribe the observed collisional behavior to the effects of collisions on the process of energy deposition in the CH_3NO_2 molecule. Collisions can strongly influence the coupling of the molecule and the IR light, e.g. by enhancing through pressure broadening the linear and non-linear IR photon absorption process. Collisionally induced R → R relaxation also helps to eliminate the effects of rotational hole burning.

3.2. Diatomic fragments

The spectrally resolved luminescence resulting from the CO_2 laser irradiation of 10 Torr CH_3NO_2 is shown in Fig. 3. Each point represents the average of 64 pulses. The spectrum shows several strong vibronic transitions of the violet $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of CN along with the 4300 Å $A^2\Delta \rightarrow X^2\Pi$ system of CH [11]. In addition, weak Swan system emission $d^3\Pi_g \rightarrow a^3\Pi_u$ from C_2 is observed. These results are in agreement with the observations of Ambartzumian et al. [3]. At low pressures the presence of these emissions was verified by the use of interference and bandpass filters.

The dynamics of the formation of the CN^* radical were followed by studying the time dependence of the B → X luminescence (isolated by a 7-51 Corning bandpass filter) using an oscilloscope with a 6 ns risetime. The maximum of the CN^* emission was achieved within the duration of the CO_2 laser pulse which was monitored by a photon drag detector.

The dependence of the B → X CN^* luminescence on CH_3NO_2 pressure was also investigated and the results are shown in Fig. 4. The luminescence intensity was measured with the help of a transient recorder at approximately 300 ns after the onset of the CO_2 laser pulse. As in the case of NO_2
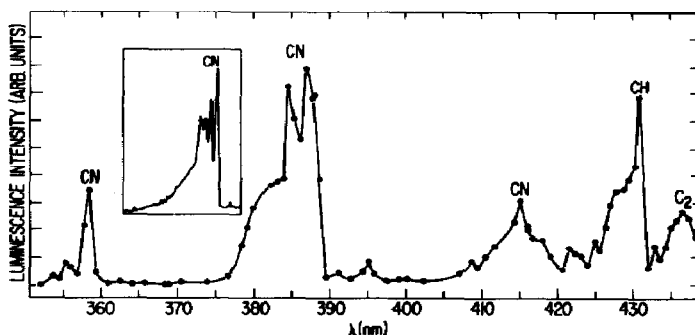
Fig. 3. Spectral distribution and assignments of the luminescence resulting from the TEA CO_2 laser (10.76 μm, 0.5 J pulse^{-1}) irradiation of CH_3NO_2 (10 Torr). Each point represents the average of 64 laser pulses. The spectral resolution is 8 Å. The inset shows the CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) emission from the CO_2 laser-induced plasma (CH_3NO_2 pressure, 30 Torr); optical multichannel analyzer detection.
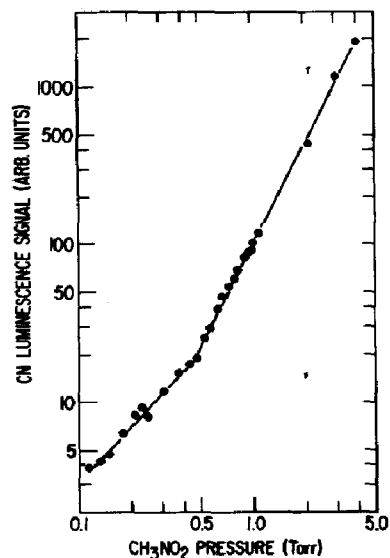
Fig. 4. The pressure dependence of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ luminescence of CN. TEA CO_2 laser at 10.76 μm (0.5 J pulse^{-1}).

and NO_2^* production discussed earlier, two distinct regimes are seen. At low pressures (below 0.5 Torr) a linear dependence ($P^{1.1}$) of the CN^* emission on CH_3NO_2 pressure is observed. Above about 0.5 Torr the dependence becomes quadratic.

The linear dependence on pressure of the CN^* emission coupled with the fast risetime is particularly important. It implies that unimolecular production of the CN radical from the CH_3NO_2 molecule occurs. Since the lowest reaction channel involves fission of the C–N bond (reaction (1)), if CN is produced from a unimolecular decomposition of vibrationally excited CH_3NO_2, CN production must involve higher lying reaction channels.

The model proposed by Ambartzumian *et al.* [3] to explain the collisionless formation of the diatomic radicals involves the accumulation of a very large amount of energy followed by the simultaneous fission of several chemical bonds. Such a mechanism appears unlikely because, although it may be characterized by a large positive entropy of activation, its activation energy should be very high. It is well known that the rate of unimolecular reactions increases rapidly with excess energy above the threshold (activation) energy [12]. Therefore a large vibrational excitation above the lowest dissociation channel is unlikely.

A reaction leading to CN and which maximizes the bonding among products, *e.g.*

$$CH_3NO_2 \rightarrow CN + H_2O + OH$$

should also be considered. Although its activation energy may not be very high, it requires a highly organized transition state which will result in a large negative entropy of activation. Therefore the reaction rate through such a channel is expected to be low and most probably will be unable to compete with the fast rate of the lowest channel.

An altogether different mechanism may involve nearby higher energy channels. For example, the fission of the N–O bond in CH_3NO_2 requires approximately 72 kcal mol^{-1}. Taking this value as a lower limit for the corresponding activation energy, this reaction channel can be only about 20 kcal mol^{-1} (approximately seven photons) higher than the lowest channel reaction (1). Since the resulting CH_3NO molecule and its rearrangement product CH_2=NOH both absorb the original CO_2 laser frequency [13], they could be further photolyzed. We could then have a mechanism which involves a moderate additional excitation to, and reaction from, a second higher lying channel followed by sequential photofragmentation of the products to finally give CN. Although the occurrence of this process cannot be proven at this point, it appears reasonable and is in line with other cases, *e.g.* SF_6, where sequential photofragmentation has been proposed [14]. Collisionless sequential photofragmentation may in fact be the mechanism for the collisionless production of C_2 observed previously [4, 5].

The pressure dependence of the CH^* emission seen in Fig. 3 was also studied. Because the emission is weaker, and because of the need to use narrow filters to discriminate against the overlapping CN^* and C_2^* emissions, the signal-to-noise ratio is low and the data are not as reliable. The pressure dependence of the luminescence is found to be $P^{1.9 \cdot 2.3}$ in the studied pressure range of 0.2 - 2 Torr. In view of the observed linear dependence at $P < 0.5$ Torr for NO_2, NO_2^* and CN^*, this result suggests that CH^* is the product of a bimolecular reaction.

The C_2^* fragment seen in Fig. 3 is obviously the result of a bimolecular reaction since CH_3NO_2 contains only one carbon atom.

Acknowledgment

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