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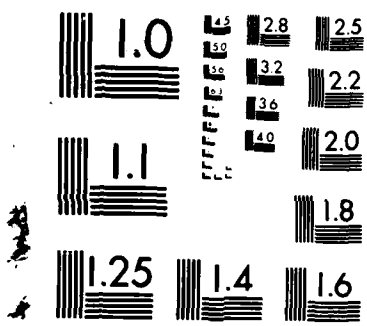

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PREDICTED NO_2 IR CHEMILUMINESCENCE IN THE NATURAL ATMOSPHERE

S. Adler-Golden
Spectral Sciences, Inc.
111 So. Bedford Street
Burlington, MA 01803

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Air Force Geophysics Laboratory
Air Force Systems Command
United States Air Force
Hanscom Air Force Base, MA 01731

"This technical report has been reviewed and is approved for publication"

ARTHUR CORMAN
Contract Manager

ROBERT R. O'NEIL, Chief
Infrared Dynamics Branch

FOR THE COMMANDER

RANDALL E. MURPHY, Director
Infrared Technology Division

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Results from the author's recent theoretical study of NO_2^* IR Chemiluminescence from the NO + O and NO + O_3 reactions are employed in a new upper atmospheric NO_2^* IR radiance model. Predictions are made for altitude-dependent and column-integrated NO_2^* chemiluminescent radiance in four vibrational bands, and comparison is made with previous model predictions.

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1. INTRODUCTION

It has been proposed that NO_2 chemiluminescence from the NO + O and NO + O_3 reactions would be a significant source of atmospheric background IR radiance in a disturbed atmosphere.[1,2] Predicting this radiance requires a reliable model of NO_2 IR emission in addition to knowledge of the species concentrations. Several radiance models have been proposed, each of which uses different assumptions and gives significantly different results. Archer's model[1] assumes a spectral intensity used in the WOE code,[3] based on "theoretical considerations of energy conservation." This spectrum gives all 3 fundamental bands a comparable intensity, and also includes numerous overtone and combination bands, resulting in substantial radiance throughout the LWIR. A second model, due to Kofsky et al.,[2,4] is based on experimental data which observes roughly a 10:1 ratio of ν_3 to $\nu_1+\nu_3$ intensity, with no other bands included. Finally, a more sophisticated, room temperature model for ν_3 and $\nu_1+\nu_3$ chemiluminescence has recently been developed by the author,[5,6] which gives excellent agreement with laboratory data at pressures in the 0.02 - 2 torr range.

In this Report a simple NO_2 IR chemiluminescence model is developed for use at the pressures and temperatures found in the upper atmosphere. The model is used to calculate radiance in the natural atmosphere in the 80 - 135 km range, where comparison can be made with the predictions of Kofsky et al.[2] Since the radiance is proportional to the NO density, the calculation may be extrapolated to the conditions of elevated NO found in a disturbed atmosphere.

The current model is based on the author's previous work,[5,6] and gives similar results at laboratory pressures. At very low pressures there are factor-of-3 differences for the ν_3 and $\nu_1+\nu_3$ bands, however, and furthermore the current model includes additional bands (ν_1 and ν_2) not included previously.

2. CURRENT KNOWLEDGE OF THE NO_2 CHEMILUMINESCENCE MECHANISM

As discussed elsewhere,[5,6] available data on NO_2 chemiluminescence is consistent with the following mechanism:

1. The NO + O reaction initially yields an activated complex that appears to possess energy equipartition between its electronic and vibrational modes. This complex relaxes either radiatively (via continuum emission) or collisionally to the ground electronic state, with vibrational equipartition maintained in either case as a consequence of chaotic dynamics in the excited electronic ($^2B_2$) state. In the low pressure limit the vibrational distribution following continuum emission is characterized by an average energy of about 5000 cm^{-1}. These conclusions are derived from the shapes and absolute intensities of the continuum and IR band spectra in the NO + O reaction.

2. The NO + O_3 reaction directly yields NO_2 in vibrational equipartition. The nascent state distribution is close to a statistical RRHO distribution, with an average energy of about 6000 cm^{-1}. These conclusions are derived from trajectory calculations[7] and are fully consistent with the shapes and absolute intensities of the continuum and IR band spectra in the NO + O_3 reaction.

3. During collisional relaxation of vibrationally excited NO_2, equipartition between the ν_1 and ν_3 modes is approximately maintained, resulting in a ~10:1 ratio of ν_3 to $\nu_1+\nu_3$ emission. This indicates that ν_1 and ν_3 quanta are collisionally removed with comparable rates. This behavior is consistent with either rapid intermode V-V coupling, or similar V-R,T rates for ν_1 and ν_3, or, as suggested by studies of vibrational deactivation in other triatomics,[8-10] a compromise between the two mechanisms. No information is available on the relaxation of ν_2. In triatomics such as O_3,[8] CO_2,[9] and OCS,[10] the rate of intermode coupling is roughly comparable to the rate of relaxation of the ν_2 mode, leading to similar effective quenching rates for all 3 vibrational modes. Similar behavior would be expected for NO_2.

4. NO_2 reacts with atomic oxygen at a rate of $0.9\text{-}1.5 \times 10^{-11}$ cm^3 $molec^{-1}$ sec^{-1}, depending on vibrational excitation. Using typical N_2, O_2 and O atom densities in the 100-135 km altitude range, where NO_2 vibrational emission should peak, and assuming NO_2 vibrational quenching rates measured in the laboratory for N_2 and O_2,[11,12] it is seen that most of the collisional removal of $NO_2(v)$ proceeds via reaction with O rather than physical quenching. This means that even if the assumption of equal quenching rates for the 3 vibrational modes is inaccurate, the impact on the column-integrated atmospheric radiance is small.

5. The Einstein A coefficients for emission are consistent with harmonic oscillator scaling rules; i.e., $A \sim v$ for fundamental bands. In this approximation, and neglecting overtone and combination bands, the rate constant for radiative removal of energy from a given mode is simply the Einstein coefficient of the v=1 fundamental.

3. MODEL DESCRIPTION

The model employs equations similar to Archer's Eq. (B-4),[1]

$$I(j) = [NO][O](k_2 + \sum_i k_{3i}[M_i])\phi(j)Q(j) \quad (1)$$

for the NO + O reaction, and

$$I(j) = [NO][O_3]k_1\phi(j)Q(j) \quad (2)$$

for the NO + O reaction, where I(j) is the radiance of band j in photons/cm^3, k_1 is the NO + O_3 rate constant, k_2 and k_3 are the 2-body and 3-body NO + O rate constants, $\phi(j)$ is the quantum yield, and Q(j) is the quenching factor, given by

$$Q(j) = A_j/(\sum_i q_i[M_i] + k_0[O] + A_j) \quad (3)$$

where A_j is the Einstein coefficient of band j, q_i is the vibrational quenching rate constant for species M_i, and k_0 is the rate of reaction with O atoms, taken as 1×10^{-11} cm^3 molec^{-1} sec^{-1}.

The rate constants k_1, k_2 and k_3 have room temperature values given previously.[5] The temperature dependences are taken from Sharp[13] for the NO + O reaction, and Borders and Birks[14] for the NO + O_3 reaction.

Assuming that 5000 cm^{-1} of vibrational energy is deposited in NO_2 in both reactions, and assuming equipartition among the 3 vibrational modes, the quantum yields are 1.1, 2.2, and 1.0 for ν_1, ν_2, and ν_3, respectively. q_i is taken as 5×10^{-13} cm^3 molec^{-1} sec^{-1} for M = O_2 and 2×10^{-13} for M = N_2.[11,12] The Einstein coefficients are taken as 110 sec^{-1} for ν_3 (Ref. 5) and 0.02 sec^{-1} for ν_2, based on the measured band strength.[15] The Einstein coefficient for the very weak ν_1 band is unknown, since a reliable

band strength is not available. For the sake of argument we take the value 0.01 sec^{-1}, which probably is an upper limit.

Unfortunately, we do not have a simple way of estimating effective quantum yields for overtone or combination bands. For the present we shall take the $\nu_1+\nu_3$ band intensity as 0.1 of the ν_3 intensity, consistent with both experiments and modeling at laboratory pressures. This ratio might change slightly under upper atmospheric conditions, however. We assume that emission from other 2-quantum bands is much smaller than $\nu_1+\nu_3$ emission, and can be neglected.

The current formulation is fully consistent with the previous model calculations[5] at laboratory pressures. However, it yields factor-of-3 smaller ν_3 and $\nu_1+\nu_3$ radiances in the low pressure limit. This is because the previous model assumed essentially instantaneous intermode vibrational mixing, causing virtually all of the emitted vibrational energy to appear in ν_3. The present model represents the opposite point of view, and assumes that the energy initially apportioned to each mode (i.e., 1/3 of the available vibrational energy) cannot be radiated by another mode. This also appears to be the point of view of the WOE spectrum used by Archer. Put another way, the previous model assumed an effective ν_3 quantum yield 3x as large, and an effective Einstein coefficient 1/3 as large. The neglect of intermode mixing in the present model means that the ν_3 radiance may be underestimated and that the predicted ν_1 and ν_2 radiances may be overestimated in the low pressure, low O atom limit. However, as explained in paragraph 4, of Section 2, the column-integrated NO_2 radiance should be insensitive to details of vibrational relaxation.

4. RESULTS

ν_1, ν_2, ν_3 and $\nu_1+\nu_3$ band radiances were calculated using the altitudes and nighttime O, NO and O_3 densities shown in Table II-3 of Kofsky et al.[2] The N_2 and O_2 densities and temperature were taken from the U. S. Standard Atmosphere.[16] The input data are given in Table 1, and the computed radiances are given in Table 2. Integrated zenith and 95 km limb radiances were computed for the ν_3, $\nu_1+\nu_3$, and ν_2 bands, and are given in Table 3 in Kofsky's units of w/km^2-sr. For the ν_3 and $\nu_1+\nu_3$ bands these values turn out to be a factor of 3 to 5 lower than Kofsky's. We note that Kofsky assumed slightly different ν_3 and $\nu_1+\nu_3$ quantum yields, and neglected $NO_2(v)$ quenching and reactive removal as well as temperature dependence of k_2. Both studies find that the contribution from the NO + O_3 reaction is negligible at these altitudes.

TABLE 1. ATMOSPHERIC INPUT DATA

Altitude/km	N_2/cm^{-3}	O_2/cm^{-3}	O/cm^{-3}	O_3/cm^{-3}	NO/cm^{-3}	$T/^oK$
80	3.0E14	8.1E13	3.E10	2.E8	8.E6	199
90	5.5E13	1.5E13	2.E11	2.E8	1.E7	187
100	9.2E12	2.2E12	5.E11	3.E7	4.E7	195
110	1.6E12	2.6E11	2.E11	2.E6	5.E7	240
120	3.7E11	4.4E10	1.E11	2.E5	3.E7	360
135	8.7E10	8.6E9	4.E10	2.E4	8.E6	517

TABLE 2. CALCULATED IR BAND RADIANCE (photons/cm^3-sec)

	NO + O Reaction				NO + O_3 Reaction			
Alt./km.	ν_1	ν_2	ν_3	$\nu_1+\nu_3$	ν_1	ν_2	ν_3	$\nu_1+\nu_3$
80	0.0	0.1	12	1.2	0.0	0.0	2	0.2
90	0.3	0.9	37	3.7	0.0	0.1	2	0.2
100	1.6	5.3	92	9.2	0.0	0.1	3	0.3
110	1.6	5.3	31	3.1	0.0	0.1	1	0.1
120	1.9	5.9	17	1.7	0.0	0.1	0	0.0
135	0.7	2.0	3	0.3	0.0	0.0	0	0.0

TABLE 3. CALCULATED COLUMN-INTEGRATED RADIANCE (w/km^2-sr)

	ν_2	ν_3	$\nu_1+\nu_3$
zenith	0.00025	0.005	0.0008
Ref. 2		0.02	0.002
95 km limb	0.008	0.2	0.03
Ref. 2		1.0	0.1

5. DISCUSSION

Although the present model uses equations similar to Archer's, and yields a similar spectrum in the collision-free limit, a very important difference is the use of different Einstein coefficients (hence, different quenching factors) for each band. This results in spectra which are strongly dominated by ν_3 and ν_1-ν_3, as predicted by Kofsky et al. The WOE-type spectrum, which shows comparable emission in all bands, is achieved only at the highest altitudes, where the intensity is weak due to the falloff of NO and O densities.

A qualitative explanation for the altitude dependence of the vibrational band radiance in the 100-120 km range is as follows. Because of the large ν_3 Einstein coefficient, this band is essentially unquenched, hence it roughly tracks the [O][NO] product, which peaks at 110 km. On the other hand, the ν_1 and ν_2 bands are efficiently removed by O atoms, hence these bands roughly track [NO], which is nearly constant at these altitudes. At lower and higher altitudes different considerations apply. At 135 km all the bands are unquenched. Below 100 km all the bands are quenched, and in addition the 3-body contribution to the NO + O reaction is important.

Since the ν_3 and ν_1+ν_3 radiances are governed by parameters which are ultimately tied to laboratory data, the uncertainty in these bands is probably comparable to the factor of 2 estimated in the previous model study of NO_2 vibrational emission.[5] The uncertainty for the ν_2 band is probably larger, since this band has not been observed in chemiluminescence. The uncertainty arises mainly in our estimate of the ν_2 quantum yield, which may lead to an overall uncertainty of perhaps a factor of 4, the lower end of the range being more probable than the higher end. The ν_1 band radiance is even more uncertain because of the unknown Einstein coefficient, but in any case it will be small enough to be of negligible importance.

The ν_3 and $\nu_1+\nu_3$ band radiances may be combined with experimental or calculated spectral shapes (e.g., Ref.5) to yield approximate radiances per micron. It should be noted that these spectra, particularly $\nu_1+\nu_3$, are broadened and red shifted from the corresponding cold bands. The ν_2 band should exhibit similar effects.

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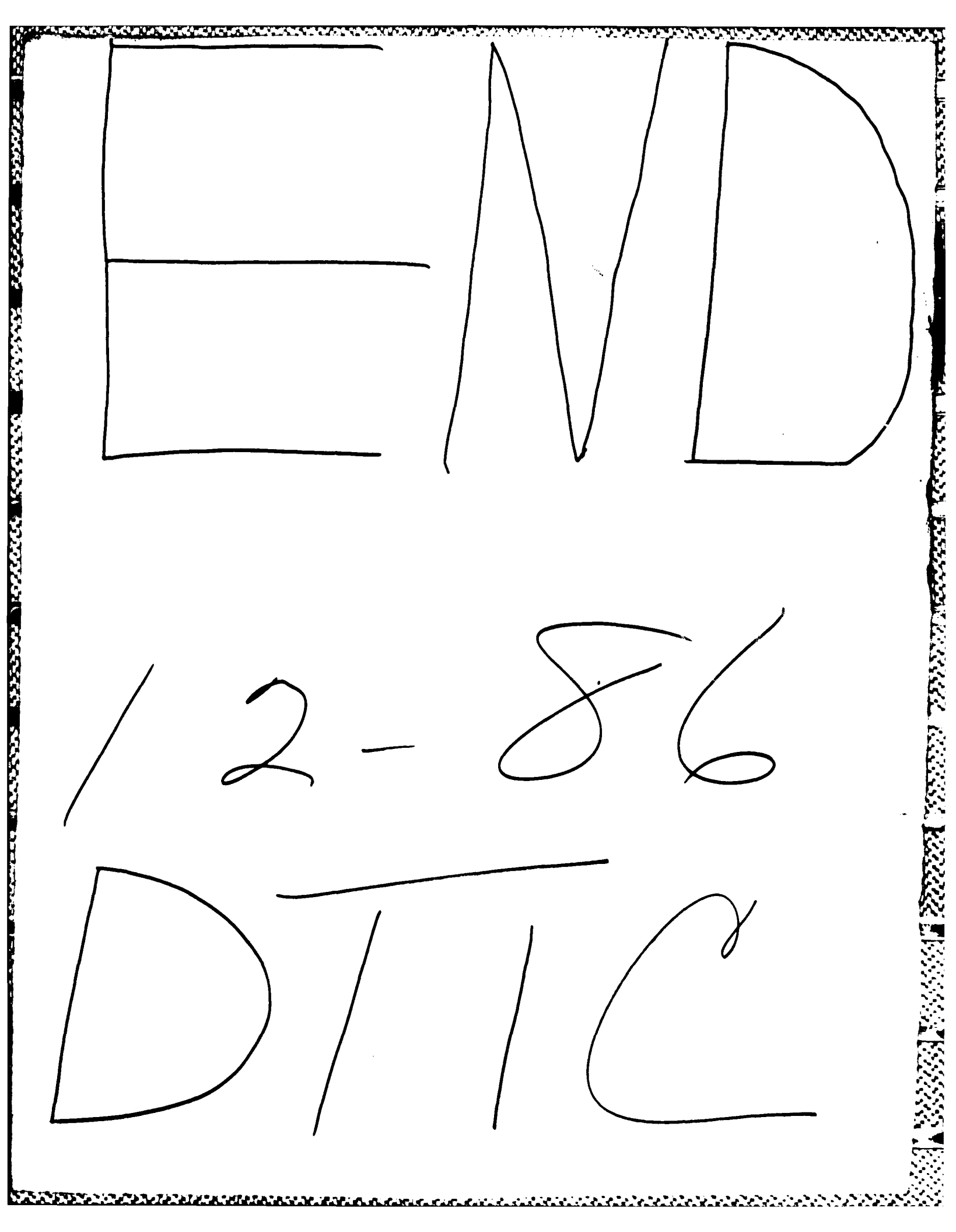
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