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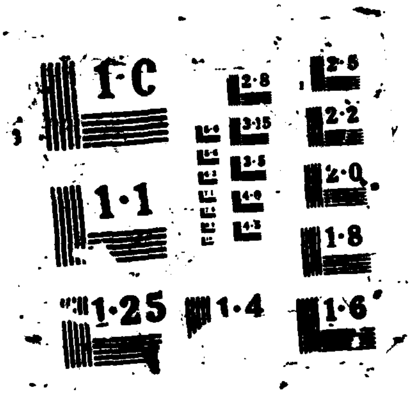
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# FILLING OF THE ATMOSPHERIC TRANSMISSION WINDOW DUE TO EMISSION FROM VERY HIGH ROTATIONAL LEVELS OF NO AND $O_3$.

16 February 1988

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## ABSTRACT

The Quantum-Mechanical Spectator Model or Impulse Approximation (IA) thus far has been used to study the collisions between fast projectiles and targets having little or no internal excitation. It is suggested that IA be applied to collisions of low energy (thermal) projectiles with targets having large internal excitation. This extension is the mechanism proposed for the R-branch bandheads observed in vibration-rotation (V-R) band emission from the high-altitude atmosphere and flow tube laboratory experiments under circumstances which rule out the presence of hot atoms. The implications of V → R transfer for radiance in the atmospheric transmission window are discussed.

## 1.0 INTRODUCTION

Recent field measurements (Espy et al. 1988, Pendleton 1987) have observed emission from very high rotation levels of NO and OH in the form of R-branch bandheads. Emission in the P-branch from these levels falls in the 6 µm high altitude atmospheric transmission window. The hypothesis advanced in this article is that very high rotational bands are produced by the collision of ambient species with highly excited vibrational levels, produced by chemiluminescent processes. If this hypothesis is correct, emission from highly excited rotational levels of $O_3$ should be observable in the 11-13 µm atmospheric transmission window.

## 2.0 VIBRATION <-> ROTATION ENERGY TRANSFER

The collisions of hyperthermal atoms with molecules have been shown to produce molecules in highly excited vibration-rotation states (O'Neill et al. 1986, Flynn and Weston 1986). Theoretically, these processes are described by quantum-mechanical impulse approximation (IA), or spectator model (Chew 1950, Chew and Wick 1952, Bogan 1974, Eckelt, Korsch and Philipp 1974, Philipp, Korsch and Eckelt 1976, Korsch and Philipp 1976, Philipp, Korsch and Eckelt 1977, and Beard and Micha 1981). In IA, the atom (C) - diatom (AB) potential is written as the sum of atom-atom potentials $V_{ABC} = V_{AC} + V_{BC}$. Eckelt, Korsch and Philipp (EKP) 1974, show that this is possible if the relative energy is above 1 eV. The incident atom C is scattered by individual atoms A and B of the molecule. Further, the time duration of the collision is much shorter than the period of vibration or rotation. The internal motion during the collision may, therefore, be considered "frozen". The momentum exchanged during the collision between the incident atom and one of two atoms of the diatomic molecule is responsible for change in the internal state of the molecule. In the formulations of IA so far considered the relative motion of A (or B) and C is due to high velocity of the incident atom C.

We now draw attention to recent experimental observations of very high rotational levels under conditions which rule out any role of hyperthermal or hot atoms. The first one is the Field-Widened Interferometer (FWI) program of AFGL, Espy et al., (1988). This program observed emission, in the 2.5 to 7.7 μm range, from an aurorally dosed high-latitude (Poker Flat, Alaska), high-altitude (> 88 km) night-time atmosphere through a zenith-looking, 1.2 $cm^{-1}$ resolution, modified Michelson interferometer. Strong emission from the fundamental ($\Delta v = 1$) VR transitions of NO around 5.3 μm was observed. The chemiluminescent part of this emission, believed due to vibrationally excited NO produced by the reaction

$$N(^2D) + O_2 \rightarrow NO(v=n) + O \qquad (1)$$

(Kennealy et al., 1978) has two components. One component, consisting of v → v-1 bands up to v = 7, is characterized by a rotational temperature of 300 $^oK$ -- the temperature of the atmosphere around 115 km altitude, which is the altitude of largest energy deposition during a moderately dosed aurora. The second component consisting of emission from R-branch bandheads for the 1 → 0, 2 → 1 and 3 → 2 VR transitions was observed at 2020, 1990, and 1960 $cm^{-1}$. We recall that the bandheads involve transitions between very high rotational levels (J' = 80.5 for 1 → 0 transition, energy about 1.3 eV). Individual rotational lines involving high rotational levels were not observed because of low signal-to-noise ratio. The bandheads could be observed only because several lines fall within a resolution element. Since no other rotational transitions were observed, it is not possible to assign a rotational temperature to this component of emission. However, in modeling studies (Espy et al., 1988) emission from bandheads does not begin to show until the rotational temperature has reached 2500 $^oK$. It is clear that there are vibrationally excited NO molecules with very high rotational excitation. Collisions would tend to establish a Maxwell-Boltzmann distribution with translational temperature. Production of very high rotational levels has to be regarded as a single collision event. Intensity in the bandhead emission is about 10 kiloraleigh (1 KR = $10^9$ photons/$cm^2$/s), compared to about 1500 KR in the chemiluminescent emission. NO at 115 km altitude, in polar atmosphere, constitutes about 0.05% of the atmosphere (Caledonia and Kennealy 1982, U.S. Standard Atmosphere 1976). Any fast atoms produced by the dissociative recombination of $NO^+$ and $O_2^+$ in an aurorally dosed atmosphere have little chance of colliding with NO before cooling down. Any mechanism involving fast atoms for the production of very high rotational levels a la O'Neill et al., 1986, has to be ruled out. It is possible that the $N(^2D)+O_2$ reaction produces a bimodal rotational distribution. A bimodal distribution for a chemical reaction may, in principle, be observed if it involves parallel abstraction and insertion/elimination pathways (Jursich and Wiesenfeld 1985), the former mechanism producing rotationally cold NO and the latter the rotationally hot NO. Another possible mechanism is the collision of vibrationally excited NO, produced by the chemical reaction, with other atmospheric species ($N_2$, $O_2$, and O), converting a large amount of vibrational into rotational energy.

The R-branch bandhead has also been detected in emissions from the hydroxyl layer (Sharma 1985) at about 85 km altitude by a ground based interferometer at Poker Flat, Alaska, by Pendleton (1987), corresponding to v' = 4 to v" = 2 transition in the ground electronic state (Meinel band) at 6505 $cm^{-1}$. The bandhead occurs for J = 10.5 and has about 1/4 eV of rotational energy. The primary source of OH emission is the chemical reaction

$$H+O_3 = OH(v) + O_2 \tag{2}$$

which populates v up to 9. The intensity of the bandhead emission is again less than 1% of the total emission in the 4-2 band. The other lines in the band have a rotational temperature equal to the translational temperature at about 85 km - about 200 $^oK$. Again parallel abstraction and insertion/elimination reaction pathways and collisional V to R energy transfer are the two viable mechanisms.

R-branch bandheads have also been observed in the AFGL cryogenic COCHISE reactor/spectrometer facility (Rawlins et al., 1988; Defaccio et al., 1986) for CO fundamental transitions ($\Delta v = 1$) when microwave-discharge excited $N_2$/Ar mixture (1-10% $N_2$; total pressure $\approx$ 1 torr at discharge) is mixed with CO. The translational temperature in the center of the reactor is about 80 $^oK$ and the pressure is 40-50 mtorr. When $O_2$ is substituted for CO, R-branch bandheads for the fundamental transitions of NO are observed. The emission from NO/CO produced by the reaction of $O_2$/CO with the microwave excited $N_2$/Ar mixture is characterized by two sets of rotational distributions: (i) cold rotational distribution with a temperature of 120 $^{\circ}$K containing v → v-1 VR bands with v up to 12 for NO and up to 14 for CO and (ii) a hot rotational distribution containing bandhead emission for v up to 4 for NO and v up to 5 for CO. The rotationally hot/rotationally cold emission ratio is about 0.2 for NO and near unity for CO - in contrast to atmospheric emission where this ratio is less than 0.01. Finally no emission is observed when CO is counterflowed in COCHISE with microwave discharge excited Ar. The discharge and the reaction region in COCHISE are separated by 10-20 cm and any hot atoms produced in the discharge region are not likely to reach the reaction region-ruling out the T → VR mechanism.

Chemical reaction is also ruled out as a possible mechanism for CO bandhead excitation - simply because no chemical reaction takes place in this instance. CO is vibrationally excited by "active" nitrogen produced in the discharge. Chemical reaction is also rendered less likely mechanism for NO bandheads when one asks why the ratio of rotationally hot/cold NO or the ratio of insertion-elemination/abstraction reaction pathways should be different in laboratory and atmosphere. It is possible that reaction of two electronic states of atomic N with $O_2$ leads to the two rotational distributions observed. However this is not a possibility in the $H+O_3$ reaction producing OH.

Intramolecular V to R transfer during a collision is thus the only mechanism which appears capable of explaining the production of high rotational levels in all the situations cited above. Theoretically this process is described by IA. It has already been pointed out that in the formulations of IA so far considered the relative motion of incident atom (C) and either of the two atoms of the molecule (B or C) is due to the velocity of C. This, however, is not inherent in the formulation (Goldberger and Watson 1964). The relative motion can also be supplied by the internal motion if (i) atoms A and/or B move fast enough and (ii) the extant of motion of these atoms is longer than the range of the repulsive forces ($\simeq$ 0.1 $A^o$) so that the atoms do not slow down due to intramolecular forces during the collision. These conditions are almost always met by OH since VR energy is manifested mainly in the motion of H atom. These criteria are also satisfied by CO and NO in highly excited vibrational states. For example, $v = 14$ level of NO in the ground rotational state has almost 3 eV of energy and the two classical turning points are about 0.6 $A^o$ apart (Gilmore 1964). The N atom moves with energy of about 1.6 eV and O atom with about 1.4 eV energy when the atoms traverse the equilibrium internuclear distance and the distance traversed by the two atoms between the classical turning points is 0.32 $A^o$ and 0.28 $A^o$ respectively. After the collision, when a large amount of V energy is converted into rotational energy, the incident atom also speeds up subject to momentum and energy conservation laws. The fast atoms thus produced ,in the laboratory but not in the atmosphere, can collide with the rotationally cold but vibrationally hot species setting up a chain which produces rotationally hot molecules. Also larger vibrational excitation would produce more intense bandheads.

Philipp et al. (1977) have studied the collisions of $Li^+$ with $N_2(v)$, $v \leq 3$ and $j = 0$, at relative translational energy of 2 eV using IA. These authors conclude; "The important result is that there is considerable energy transfer between translational and vibro-rotational degrees of freedom, but no transfer from vibration to rotation". These authors define energy transfer

$$\overline{\Delta\epsilon} = \Big(\sum_{v;j'} \Delta\epsilon \; d\sum_{v;j'} / d\Omega(v'j' \leftarrow v0)\Big) \Big/ \Big(\sum_{v;j'} d\sigma/d\Omega(v'j' \leftarrow v0)\Big) \qquad (3)$$

quantity one would more reasonably call <u>average</u> energy transfer. It is clear from Figure 1 of PKE that for $v > 0$ and $\Delta\epsilon < 0$, i.e., when translational energy increases, rotational resonances corresponding to V to R energy transfer are observed. Further, as v increases these resonances become more broad indicating that a larger amount of energy is being transferred from V to R. There is great deal of cancellation between positive and negative components of $\overline{\Delta\epsilon}$, with the result that average energy transfer is independent of v. The conclusion then should have been: Although a great deal of energy may be transferred between vibration and rotation in individual collisions, on the average, in hyperthermal collisions, no energy is transferred from vibration to rotation. For thermal collisions involving a highly excited vibrationally and/or rotationally excited molecule, this conclusion may not hold because of the lack of energy transfer from translational to internal degrees of freedom. That the rotational energy can also be converted into vibrational energy may easily be seen from Figure 5 of PKE. The top panel shows a plot of a differential cross section at scattering angle of $90^o$ for $N_2$-$Li^+$ collision as a function of final state of the molecule, the initial state being j = 34 and v = 0. The threshold for exciting v = 2 level is seen to be lowered from 0.584 eV to about 0.35 eV showing that nearly 0.23 eV out of 0.30 eV of R energy is converted into V energy. While the work of PKE shows that it is possible to transfer energy from V <-> R in individual hyperthermal collisions, we believe we have shown that this process is capable of explaining the experimental data, outlined above, for the bandhead formation in the thermal collisions of highly excited vibrational species.

Stewart et al. (1988), in a recent publication, have reported the observation of large cross-sections ($\rightarrow 8\ A^{o2}$) for v → R process during collision of VR excited $Li_2(A\sum\limits_{u}^{1+})$ with Ne.

## 3.0 RADIATION IN THE ATMOSPHERIC TRANSMISSION WINDOW DUE TO EMISSION IN THE P-BRANCH OF VERY HIGH ROTATIONAL LEVELS

Figure 1 shows emission spectra of 1 <-> 0 5.3 $\mu m$ VR band of NO at 5 $cm^{-1}$ resolution and at rotational temperatures at 200 $^oK$ and 10000 $^oK$. Both spectra have the same integrated radiance. Additional rotational lines were incorporated into the spectrum than are available on the AFGL linefile. Figure 2 shows emission from NO around 5.3 $\mu m$ from a gas with bimodal rotational distribution with a fraction of the hot component being 1% and the temperature 1000 °K. The resolution again is 5 cm$^{-1}$. The emission from the hot component near the band origin is about two orders of magnitude smaller than that from the cold component and flat down to 6.5 µm. The idea is that the radiance is very much enhanced in the window region due to the P-branch of the highly excited rotational states. The concept of V <-> R transfer has not been tested for triatomic molecules. Assuming that the concept holds, it is natural to inquire if the radiance levels are enhanced in the 11-13 µm transmission window due to rotationally hot $O_3$ around 10 µm at rotational temperature of 200 °K. Figure 4 shows the spectrum of $O_3$ with a rotational temperature of 10000 °K. As can be seen from the figure, there is a decided increase of radiance towards the window region. The spectrum cuts off abruptly because the AFGL linefile does not contain very high rotational levels. The issue of spectroscopic constants which yield accurate line positions for high rotational levels is being pursued.

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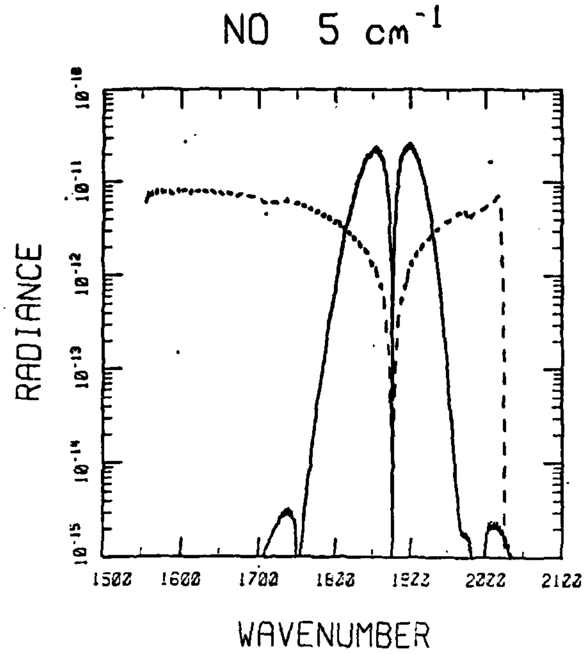

Figure 1. Nitric Oxide, 5 $cm^{-1}$ Resolution, at Rotational Temperatures 200 °K (Solid Line) and 10000 °K (Dashed Line).

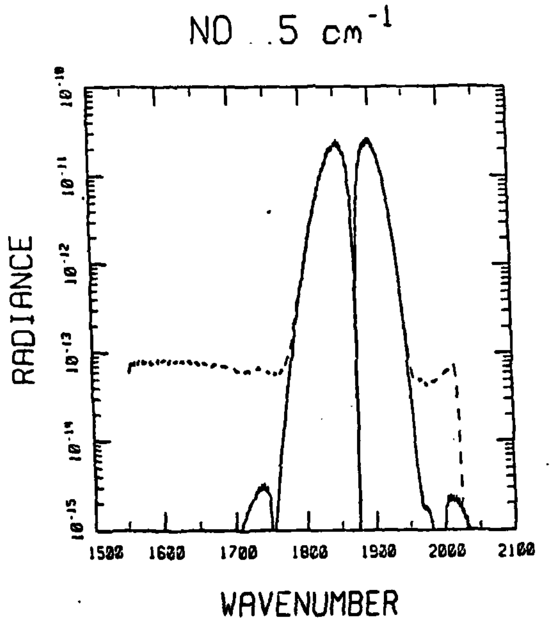

Figure 2. **Emission from Cold NO at a Temperature of 200 °K. The Dashed Lines show a Bimodal Rotational Distribution Whose Hot Component is 1% NO at a Rotational Temperature of 10000 °K.**

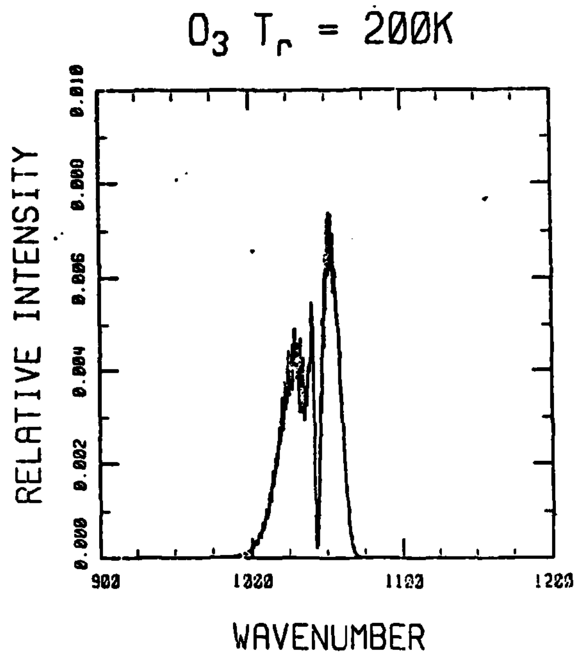

Figure 3. **Emission from Rotationally Cold (200 $^{o}$K) Ozone Around 10 μm.**

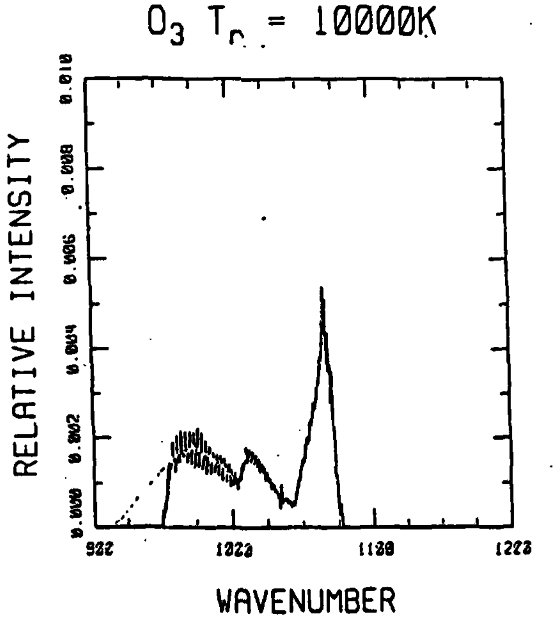

Figure 4. **Emission from Rotationally Hot 10000 $^{o}$K Ozone Around 10 μm. The Dotted Lines Indicate the Estimated Contributions of High J Lines not Included in this Calculation.**

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