Millimeter-wave optical double resonance spectra of NO$_2$: How good a quantum number is $N$?

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Optical transitions to the $^2B_2$ electronic state region of NO$_2$ have been observed in double resonance with three millimeter-wave ground state rotational transitions. The probed ground state transitions were the $N = 2$ ($F_1$), $N = 4$ ($F_1$), and $N = 10$ ($F_2$), $K = 0 \rightarrow 1$ $Q$ branch transitions near 250 GHz. The optical range scanned was 16 800 to 16 950 cm$^{-1}$. The $10_{0,10} - 9_{0,9} F_1$ spectrum was combined with previous double resonance results with the ground state $9_{1,9} - 10_{0,10} F_1$ transition. This comparison shows 70 out of 160 upper states with $J = 19/2$ to have indefinite or mixed $N$ values. It establishes violations of the $\Delta N = \Delta J$ selection rule in this spectral region which contains bands with a wide range of spin-rotation constants. Lack of intensity correlation between the two spectra suggests two classes of upper states are present: a group of strongly $N$-mixed upper states, and a group essentially unmixed in $N$. Heller's $F$ parameter, which measures the fraction of all possible symmetry-restricted basis states contributing to a typical eigenstate, is similar for the double-resonance spectra of the three $N$ values, but is greater for $K = 1$ than for $K = 0$. By finding upper states in common, $R$ lines from $N = 2$ and $P$ lines from $N = 4$ have been identified.

The NO$_2$ optical absorption spectrum is a near-continuum in the $^2B_2$ state region studied here and in the previous paper. Evidence suggests that this complexity is largely due to coupling between vibrationally excited states of the ground electronic state and the much sparser vibrational states of the $^2B_2$ electronic state. Hardwick$^3$ observed that the spectrum is more complicated than expected even for complete mixing of all vibronic states of the same symmetry. He conjectured that this extra complexity results from quantum ergodicity in the manifold of vibrationally excited ground electronic states, that is, the eigenstates are mixtures of all basis functions of a given total symmetry regardless of vibrational, rotational, or electron spin quantum numbers. This implies a corresponding breakdown in vibronic, $N$ (rotational angular momentum), and $K_a$ selection rules, although $J = N + S$ remains a good quantum number because of the weakness of the hyperfine coupling (see Ref. 1).

Ergodicity in quantum and mechanical and classical systems has been discussed by Heller$^1$ and others. For systems in which the initial state is “localized” in phase-space, Heller has proposed a quantum mechanical measure of ergodicity $F$ which may be interpreted as the fraction of available phase-space that is accessed by the dynamics of a given initial state. When that fraction is large, the initial state samples much of the available phase-space, and is thus ergodic. In both classical and quantum mechanics, the definition of available phase-space depends on perceived symmetry properties of the system and the corresponding constants of the motion. In classical dynamics, a number of constants of the motion may be specified equal to the dimensionality of the system. Classical trajectories trace out the invariant torus of the motion, and cover the accessible phase space uniformly for almost all trajectories. In quantum dynamics, additional discrete symmetries reduce the available phase space to states of the same eigenvalue with respect to that symmetry. Breakdown of symmetry via perturbations changes the available phase-space, but only if the splittings are greater than the experimental resolution. Because quantum mechanical wave functions have nodes, the $F$ parameter cannot reach the value 1. A state in which eigenstates have a Gaussian random distribution of overlap with each accessible basis state has been suggested as an archetype of a quantum mechanical ergodic state. This state has an $F$ value of 1/3.

Further, quantum dynamics only follows classical dynamics for a time on the order of the inverse of the density of states. Experimental spectral resolution may also limit the accessible time scale.

In the excited states of NO$_2$, Hardwick has suggested that only the overall rovibronic symmetry and $J$ are preserved; that eigenstates are random mixtures of all vibronic, rotational, and electron spin basis states with specific values of $J$, total symmetry, and energy. This hypothesis defines a phase-space over which ergodicity can be measured using Heller's $F$ parameter. When the absorption spectrum in a given region can be attributed to a small number of basis functions and thus is localized in phase-space, we can use an experimental line spectrum to determine how ergodic those basis functions are. The existence of some approximately good quantum number beyond those assumed in defining the density of states would imply a measured $F$ value smaller...

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than 1/3. The degree of ergodicity results from off-diagonal coupling between the basis states, and thus may be a function of conserved or partially conserved quantum numbers in the system.

Double resonance is capable of reducing the complexity of the optical spectrum to a set of resolved lines originating from specific ground state levels. In Ref. 1, we used microwave detected, microwave-optical double resonance to determine the degree of quantum ergodicity in the energy region \( \sim 17 \, 000 \, \text{cm}^{-1} \) above the ground state of NO_2. We recorded the optical double resonance spectra from the two ground state rotational levels \( N_{0,0}, K_r = 9_{1,9} \) and \( N_{1,0}, K_r = 10_{0,10} \) \( (J = N + 1/2; F = J + 1) \). The number of transitions observed was much greater by a factor of 8 than would be expected if \( N \) and \( K_r \) were good quantum numbers in the upper state, but fell short by a factor of 3 from matching the number predicted by Hardwick's ergodicity conjecture. We have repeated that experiment with significantly improved dynamic range, and found the number of observed transitions to increase to 40% of that predicted. The observed \( F \) value is about 0.2 and changes little with the increase in the number of transitions due to intensity factors in the expression for \( F \). The \( F \) value and number of observed transitions is consistent with \( N \) but not \( K_r \) remaining a good quantum number. In Ref. 1, we presented arguments for and against \( N \) breakdown. Against \( N \) breakdown, we argued that the spin-rotation terms in the Hamiltonian coupling different values of \( N \) are probably small compared to the mean level spacing, and thus \( N \) should remain approximately a good quantum number. By this we mean that most of the strong lines should obey the \( \Delta N = \Delta J \) selection rule. Previous experiments had established violations of the \( \Delta N = \Delta J \) selection rule, but these experiments did not determine the extent of the breakdown of \( N \) as a quantum number for typical excited eigenstates. If \( N \) remains largely a good quantum number, then Hardwick's conjecture overestimates the available phase space by a factor of 2. Then the experimentally determined \( F \) should be reported as 0.4, implying nearly ergodic mixing over the other quantum numbers. We noted in Ref. 1 that further double resonance experiments on a greater variety of NO_2 ground state transitions could test for specific characteristics of the optically accessed upper states such as \( N \) breakdown, or the \( F \) dependence of \( F \).

In this work, we have extended the double resonance experiments to other lower states by using millimeter-wave (mm-wave) radiation in the 250 GHz region where the NO_2 \( K = 0 \) branch occurs. We believe this is the highest frequency at which mm-wave-optical double resonance has been performed. The probed transitions were the \( 2_{0,2} - 2_{1,1} \) \((F_r, F = J + 1)\), the \( 4_{0,4} - 4_{1,3} \) \((F_r, F = J + 1)\), and the \( 10_{0,10} - 10_{1,9} \) \((F_r, F = J + 1)\), with assignments and frequencies taken from Bowman and DeLucia. The optical region from about 16 800 to 16 950 cm\(^{-1}\) was scanned for each mm-wave transition.

The \( F \) component of the \( N = 10_{0,0} - 10_{1,9} \) transition was selected so that the \( 10_{1,9} \) level would have the same \( J = 19/2 \) as the \( 9_{1,9} \) level probed in Ref. 1. As part of a study of statistical properties of NO_2 energy levels, we have recorded the \( 9_{1,9} \) spectrum with improved experimental conditions. If \( N \) were a good quantum number in the upper state, transitions from the two \( J = 19/2 \) lower states would access disjoint sets of upper states. Upper states in common must be states of mixed \( N \), containing significant character of \( N = 8 \) and 9 for \( P \) lines, or \( N = 10 \) and 11 for \( R \) lines. In the limit of complete mixing, all upper states seen in one double resonance spectrum would also be seen in the other. We observed 70 out of 160 upper states to be of mixed \( N \).

The \( N = 2 \) -- 2 and \( N = 4 \) -- 4 transitions were selected to observe the variation with \( N \) of the double resonance line density, and to allow identification of \( P \) and \( R \) lines by matching upper states. The branches of some lines were identified, but signal to noise problems prevented a complete separation into \( P \) and \( R \) lines. We found that Heller's \( F \) parameter decreased slightly with increasing \( N \). In addition, the \( K = 1 \) states show greater ergodicity, as measured by \( F \), than the \( K = 0 \) states, suggesting Renner--Teller coupling to the \( ^2A_2 \) state, as mentioned by Brand et al.\(^5\).

**EXPERIMENTAL TECHNIQUES**

The double resonance setup used here is similar to the microwave detected MODR experiment described in Ref. 1, with some changes for the mm-wave probe field. Methods and frequency multipliers developed at Duke University were used to generate the mm-wave radiation as harmonics of lower-frequency phase-locked klystrons. The \( 10_{0,10} - 10_{1,9} \), \( J = 19/2 - 19/2 \), \( F = 21-1/2 \) transition at 246.514 MHz was reached by tripling a Varian of Canada VRB-2113B klystron producing about 250 mW of fundamental power. The other two transitions, the \( 2_{0,2} - 2_{1,1} \), \( J = 5/2 - 5/2 \), \( F = 7/2 - 7/2 \) transition at 22.9067.49 MHz and the \( 4_{0,4} - 4_{1,3} \), \( J = 9/2 - 9/2 \), \( F = 11/2 - 11/2 \) transition at 231.229.96 MHz were reached by quadrupling an OKI 55V11 klystron producing 500 mW of fundamental power. After passing through a high-pass filter and through transitions to WR-42 waveguide, the radiation was propagated quasioptically. A mitered right angle rather than a curved \( E \) plane bend coupling to the sample cell reduced mm-wave reflections, and allowed the focused laser pulse to enter through a small hole in the mitered face. At the cell exit, the defocused laser light was blocked by a 1/2 in. thick Teflon block which was transparent to the mm-wave radiation. The mm-wave detector was a Coehsice Instruments liquid He cooled InSb detector with a submicrosecond rise time.

The Nd--YAG pumped dye laser system was described in Ref. 1. The dye laser output with an intracavity etalon had a linewidth of about 0.04 cm\(^{-1}\), and produced 15 mJ pulses at a 20 Hz repetition rate. The dye used was Kiton Red (Exciton). The laser was SF_6 pressure scanned over successive 11 cm\(^{-1}\) spectral regions with frequency calibration determined from the I_2 fluorescence spectrum. The accuracy of measured line frequencies is estimated to be 0.015 cm\(^{-1}\). Many of the NO_2 optical lines were saturated, but the mm-wave power was far below saturation because of the low power available, and because of the small dipole moment of NO_2. The resulting low Rabi frequency made the transient rotation signals several microseconds long, limited by Doppler dephasing at low pressure. The maximum sample pressure was limited by rotational relaxation which damped
the signal. The optimum pressure was about 75 mTorr of NO₂. The transient nutation signal was detected with a boxcar set with a gate width of 1.5 μs, beginning 1 μs after the laser pulse. A time constant of 1 s was used in recording the scans. It was essential to flow the NO₂ rapidly through the sample cell because of laser-induced decomposition.

EXPERIMENTAL RESULTS

Sample double resonance scans are shown for each of the three probed transitions in Fig. 1. Optical transitions that pump the lower, K = 0, rotational levels caused decreased probe absorption (downward), and conversely for K = 1. As discussed in Ref. 1, the strongest optical transitions are quite saturated. The line pedestals are caused by wings on the laser frequency distribution accentuated by saturation of the peak of the line. Table I lists the spectral ranges covered, number of transitions observed, and the maximum signal/noise ratio for each N value. Table I also lists the results from the new 100-9,9 scans as well as 80,8-7,7 scans to be reported as part of statistical analyses in a later publication.5 Figures 2, 3, and 4 show the stick double resonance spectra for the three mm-wave transitions probed. Lines identified as P or R branch transitions as discussed below are also indicated by marks at the graph borders. The dynamic range was poorest for the N = 4-4 transition because the least mm-wave power was generated at that frequency. Tables of the frequencies and intensities of all observed transitions from the sampled states are available from PAPS.7

DISCUSSION

How good a quantum number is N?

The rotational levels in the ground vibronic state of NO₂ are states of definite N to a high level of approximation (with a few well known exceptions).3 Ground states with N values of 9 and 10 but the same J value of 19/2 have been studied in double resonance. These states are the K = 1 components of the two transitions, 9₁₉₋₁₀₀ at 40 661.44 MHz and 10₀₋₁₀₁₉ at 246 541.12 MHz. Since J = N + S (S = 1/2), two values of N are possible for each J. When N is a good quantum number, the spectrum follows the optical selection rule ΔN = ΔJ. In that case, the sets of upper states accessed from states of the same J but different N are disjoint. Although allowed R branches from the 9₁₉ state reach states of the same N as Q branches from the 10₁₀ state, these transitions reach states of different J. These pairs of states differ in energy by a spin-rotation splitting, seen by Smalley et al.8 to be on the order of 0.5 cm⁻¹. Moreover, the parallel band Q branch Hön-London factors are about 1/50th of the P or R branch factors for these values of N and K_a, so few of the observed optical lines are expected to be Q branch transitions, especially in our 10₁₀, F₉ spectrum, due to limited dynamic range. The upper states carrying P and R branch intensity from the 9₁₉, F₁ state are J = 17/2, J = 8, K_a = 1 and J = 21/2, N = 10, K_a = 1, and from the 10₁₀, F₂ state are J = 17/2, N = 9, K_a = 1 and J = 21/2, N = 11, K_a = 1.

If each upper eigenstate, with a given J, contains contributions from the two basis states with N = J ± 1/2, then transitions to those states would be observed from each
NO$_2$ Double Resonance Spectrum

2(0,2) $F_1$ → 2(1,1) $F_1$ Transition

FIG. 3. Double resonance stick spectrum for the 2(0,2)→2(1,1), $J = 5/2$, $F = 7/2$ transition at 229 067.49 GHz. $R$ lines identified by matching upper states with $N = 4$ are marked at the graph edges.

ground state level, separated by the ground state energy difference of 9.600 cm$^{-1}$. If the $N$ mixing is weak, such that each eigenstate is dominated by basis states of one $N$ and has only small overlap with states of the other, then one expects a strong anticorrelation of the intensities of the lines in the two spectra. If a transition is "allowed" in one spectrum it will be "forbidden" in the other and vice versa. In the limit of full ergodic mixing of different $N$ states, one expects the overlap of the two $N$ states to be random, and thus the intensities will be independent distributions, that is, will be uncorrelated.

Over the 158 cm$^{-1}$ upper state energy range scanned for both MODR transitions, 160 lines were observed from the $N = 10$ level, and 284 lines from the $N = 9$ level (using the improved $N = 9$ dataset, Ref. 5). To search for states of mixed $N$, we required upper state energies from the two datasets to match within 0.02 cm$^{-1}$. Seventy matches were found. Statistics for two independent distributions predict 18 spurious matches due to the finite acceptance windows. A similar number of potential matches is expected to be lost due to overlapping lines in the spectra. Thus the number of identified upper states of mixed $N$ is about 70. The $N = 9$ spectra have a high signal to noise ratio, and the number of observed lines increased only modestly with a factor of 4 increase in S/N. Except for problems of overlapping lines, all transitions with greater than 5%–10% of the average line intensity were observed, depending on how the correction for saturation is made. Failure to observe a match for a transition seen in the $N = 10$ spectrum implies that the corresponding excited eigenstate has less than 10% as much overlap with the basis functions that carry intensity from the $9,1,9$ lower state as does the average upper state observed in the $N = 9$ spectrum. Furthermore, because the number of observed lines requires $K$ to be strongly mixed for most upper states, the average upper eigenstate has only a fraction of its basis states with the correct $K = 1$ character to be sampled by the optical transition. The amount of $N,K_a = 1$ should be similar in all states with the same $N$, about 1/5 in this case for complete mixing, conserving symmetry. We conclude that lines observed in the $N = 10$ spectrum (with $N = J - 1/2$) and not matched in the $N = 9$ spectrum have on average less than 10% total $N = J + 1/2$ character. We call these states of definite $N$.

Since over half of the states observed in the $N = 10$ spectrum are of definite $N$, it is natural to expect that even for those states of indefinite $N$, each eigenstate will be predominantly of one $N$ or the other. In that case, there would be an anticorrelation of the intensities for the matched lines in the two spectra. A scatter plot of the intensities for the matched lines is shown in Fig. 5. No strong anticorrelation of the intensities is evident. A further measure may be defined by

Distribution of Intensities to Upper States of Indefinite $N$

FIG. 5. Scatter plot of intensities to the 70 upper states reached by transitions from $N = 9$ and $N = 10$ lower states, both with $J = 19/2, F = 21/2$. Since the lower states are essentially unmixed in $N$, the upper states are of indefinite $N$. 


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\[ C = \langle I_1 I_2 \rangle / \langle I_1 \rangle \langle I_2 \rangle, \] where \( I_1 \) and \( I_2 \) are the line intensity in the two spectra, and the averages are over the matched lines only. This statistic should be close to zero for strongly anti-correlated intensities, but near 1.0 for uncorrelated intensities as expected for ergodic mixing. The observed value is \( C = 0.92 \), indicating at most a small amount of anticorrelation. The lack of correlation suggests that the upper states are of two classes, a few that are strongly mixed in \( N \), and the majority that are essentially unmixed. Because each double resonance spectrum shows an average intensity of matched lines close to the average of all lines, the two classes have similar absorption strengths. The intensities used here are uncorrected for saturation, blending, and limited dynamic range, so this conclusion should be considered tentative.

Two other searches for upper state matches were made to test the statistical assumptions and the consistency of the data. Upper state matches were found between the \( 10_{0,10} F_1 \) and \( 10_{0,10} F_2 \) states, and between the \( 10_{0,10} F_2 \) and \( 10_{1,9} F_2 \) states. In the first case, matches are forbidden because \( J \) is a good quantum number, and in the second because the states have different rovibrational symmetry. In both cases the number of matches was just about the same as the number expected for randomly distributed lines with our acceptance window of 0.02 cm\(^{-1}\). The definitive confirmation of \( N \) breakdown provided by double resonance is necessary. In a perturbed spectrum of this type there is no model Hamiltonian to provide a final confirmation of line assignments and intensities. Hallin and Merer reported that they were able to assign nearly all the strong lines without invoking \( N \) breakdown. Perrin \textit{et al.} are thus assigning the weaker lines to forbidden transitions in a spectrum with a line approximately every 0.1 cm\(^{-1}\), where the full linewidth is 0.035 cm\(^{-1}\). Camy-Peyret\textsuperscript{11(c)} reports that their window criterion for matching upper state energies was 0.007 cm\(^{-1}\). This is a stringent criterion, and many of their forbidden line assignments are probably correct, but others may be accidental coincidences with lines from other vibrational states which borrow less intensity from the \( ^2B_2 \) electronic state.

### Transitions from the low \( N \) states

Double resonance experiments were performed on the \( 2_{0,2} \rightarrow 1_{1,1} F_1 \) and the \( 4_{0,4} \rightarrow 4_{1,3} F_1 \) transitions to observe the variation in line density with \( N \) and to identify \( P \) and \( R \) branch optical transitions by finding lines which access the same upper states. Success of the sorting into \( P \) and \( R \) branches would have allowed us to examine energy level spacing statistics, one of the proposed tests of "quantum chaos." The upper states accessed by lines from both spectra will have \( J = 7/2 \) because they are reached by \( R \) lines from the \( N = 2 \) \( F_1 \) states and by \( P \) lines from the \( N = 4 \) \( F_1 \) states. The unmatched lines may contain some \( K = 1 \) \( Q \) branch transitions for \( N = 2 \) because this Hann–London factor becomes significant for such low \( N \) values. For the \( K = 0 \) states, the unmatched upper states should consist of \( J = 3/2 \) states from the \( 2_{0} \) spectrum, and \( J = 11/2 \) states from the \( 4_{0} \) spec-
TABLE III. Application of statistical tests for quantum ergodicity to the double resonance results. See the text for discussion. Last four lower states are taken from Ref. 4.

<table>
<thead>
<tr>
<th>Lower state</th>
<th>Vibr. state density</th>
<th>Good quantum numbers</th>
<th>Line density (per cm⁻¹)</th>
<th>Observed</th>
<th>Heller's F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>J,N,Kₜ</td>
<td>J,N,J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(0,2) F₁</td>
<td>0.075</td>
<td>0.15 0.45 0.90</td>
<td>0.335</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>2(1,1) F₁</td>
<td>0.075</td>
<td>0.225 0.675 1.35</td>
<td>0.561</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>4(0,4) F₁</td>
<td>0.075</td>
<td>0.15 0.75 1.5</td>
<td>0.312</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>4(1,3) F₁</td>
<td>0.075</td>
<td>0.15 0.75 1.5</td>
<td>0.375</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>10(0,10) F₂</td>
<td>0.075</td>
<td>0.15 1.65 3.3</td>
<td>0.703</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>10(1,9) F₂</td>
<td>0.075</td>
<td>0.15 1.65 3.3</td>
<td>0.966</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>7(1,7) F₁</td>
<td>0.075</td>
<td>0.15 1.20 2.4</td>
<td>1.677</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>8(0,8) F₁</td>
<td>0.075</td>
<td>0.15 1.35 2.7</td>
<td>1.459</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>9(1,9) F₁</td>
<td>0.075</td>
<td>0.15 1.50 3.0</td>
<td>1.668</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>10(0,10) F₁</td>
<td>0.075</td>
<td>0.15 1.65 3.3</td>
<td>1.525</td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

The failure to achieve the expected match of approximately half the lines from the lower signal/noise group is surprising because both the P and R branch transitions derive their intensity from the 3₁,0 or 3₁,2 character of the upper state. Since all the optical transitions are part of parallel bands, interference between different transition moment components is not possible, so that the P/R intensities should maintain a constant ratio. Even noting that Q branch transitions are of observable strength in the 2₁,1 case does not greatly improve the result. The failure is most likely due to the poor signal/noise in both spectra; lines with small S/N could easily have been missed.

The same type of statistical analysis applied to transitions from the 10₀,₁₀ F₁ state in Ref. 1 may be applied to these data. With a calculated density of vibrational states of 0.075/cm⁻¹ for each symmetry species, if J, N, and Kₜ are all good quantum numbers in the upper state, we expect 0.15 double resonance lines/cm⁻¹ if only P and R branch lines are observable, or 0.225 lines/cm⁻¹ if Q lines are also observable. If Kₜ or N are mixed, the predicted number increases, as shown in Table III. The observed densities are consistent with N remaining a good quantum number. As shown in Fig. 6 for the N = 10 data, and in Ref. 1 for the earlier data, the distribution of line intensities is strongly peaked at low intensity. The number of observed lines thus depends strongly on the experimental dynamic range, and is not a reliable measure. Heller's F parameter, measuring the degree that a given basis state is spread over all accessible eigenstates, varies little when additional weak lines are added to the data set. The values of F for these data, as well as the new data on the 10₀,₁₀ F₁, 9₁,₉ F₁, 8₀,₉ F₁, and 7₁,₇ F₁ states are shown in Table III. The observed values, with the exception of the N = 4 states which had very poor signal/noise, display a slow decrease in F with increasing N, with none of the values very different from the previous value of 0.20 for 10₀,₁₀ F₁ reported in Ref. 1. The K = 1 states have a higher line density and thus have higher F values than the K = 0 states. The most likely explanation for this effect is the existence of additional coupling terms in the Hamiltonian that are proportional to Jₓ, and thus are zero for K = 0 states. An interaction of this type is Renner–Teller coupling to the 2A₂ state, which has already been suggested by Brand et al., to explain intensity anomalies in lower energy bands. Double resonance on higher K states could test this hypothesis.

CONCLUSIONS

We have extended the double resonance experiments reported in Ref. 1 by performing mm-wave optical double resonance experiments for six lower state levels. This new data...
gives two principal conclusions.

First, comparison of spectra from levels with the same value of J but different values of N, demonstrates that at least 70 out of 160 upper states were of mixed N. This result was unexpected for reasons advanced in Ref. 1. The present result leads to the conclusion that N is significantly but not totally broken down as an approximately good quantum number. Breakdown of the N selection rules has been reported by previous authors, but this is the first experiment that allows the degree of N breakdown to be measured for a large number of typical eigenstates. Taking into account the existence of a weak selection rule on N still operating, the degree of ergodicity over the other degrees of freedom is increased. When computing Heller's F value, one divides the number of states consistent with the known good quantum numbers. We thus anticipate that the F value for delocalization over states of the same N, corresponds to a number on the order of 0.31, greater than the 0.20 computed for delocalization over all states. It is not simply a factor of 2 higher (the number of possible values of N) since one must also subtract off one-half of the estimated number of transitions of mixed N from the observed transitions. Since the F value expected for an ideal ergodic distribution is 1/3, we see that the present results are consistent with a completely ergodic distribution over vibronic states and K_a, but only a small degree of ergodicity over N. The physical explanation for even this small degree of N mixing is unclear, given the small value of the spin-rotation constants observed in most of the excited states that have been rotationally analyzed.

The second result is that the degree of ergodicity observed in the Z_02 is similar to that observed for the 10_010 and 8_084 states. This may result from a balance of two factors. The Coriolis operator which couples basis states of different K_a is linear in angular momentum, and thus grows with J. The centrifugal distortion operator, which also couples basis states of different K_a grows as J^2. Opposing this, the range of K_a that must be mixed to achieve ergodicity also grows with J. Classically, in ergodic rotational motion the amount of energy that is exchanged between the rotational and vibrational degrees of freedom is (A-C)J^2, where A and C are the rotational constants. Ergodicity, or the fraction of available phase space which is accessed, is distinct from the number of observed transitions, which does increase with J, and from the rate at which energy spreads out of the initially prepared state, which is related to the width of an individual resonance feature, not the number of lines it contains.

The present results add to our understanding of the excited eigenstates of NO_2. When eigenstates are strongly mixed over many basis states, double resonance provides a way of simplifying the spectrum and a template to characterize the eigenstates. To the extent that double resonance can be performed on the full range of quantum numbers that may be mixed, the eigenstates can be reconstructed in terms of basis functions. The present mm-wave experiments give more flexibility than microwave experiments alone. Still, in NO_2 the accessible low J levels are restricted to K_a = 0 and K_a = 1. The present experiments, even with this restriction, have clarified the extent of intramolecular energy redistribution in NO_2. Additional double resonance experiments which allow the sampling of all thermally populated values of K_a would further enhance our understanding of the NO_2 spectrum.

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7See AIP document no. PAPS JCPSA-85-4297-13 for 13 pages of observed MODR transitions in NO_2. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche ($5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.