

Observation of high- l Rydberg states of nitric oxide

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We report the observation of the $5g\text{-}4f$ Rydberg-Rydberg infrared transition of nitric oxide at 2500 cm^{-1} using high-resolution (0.03 cm^{-1}) Fourier-transform spectrometry. A rotationally cold (70 K) and resolved spectrum has been obtained in emission from a supersonic jet discharge. A spectrum emanating from hot (850-K) NO gas has also been observed. This spectrum exhibits characteristic spikes reflecting the quantization of the electron angular momentum along the axis of fast core rotation. Both spectra are quantitatively reproduced by theory. The manifestation of "circular" states in the hot spectrum is discussed.

High-orbital-angular-momentum states, although commonly observed in atomic spectroscopy,¹ have only rarely been identified in molecules. Thus far, diatomic hydrogen has been the only molecule for which Rydberg states with $l \geq 4$ have been observed under high resolution.²⁻⁵ The reasons for the general lack of knowledge concerning such states in molecules are related to the presence of the internal nuclear (rotational and vibrational) degrees of freedom. Highly excited states in molecules are basically less stable than corresponding atomic states, since radiationless decay processes (predissociation and preionization) are in competition with the radiative decay routes. The thus decreased lifetimes of molecular states render the excitation of high- l states (e.g., in stepwise processes) more difficult.⁶ Even when excited, molecular high- l Rydberg states are not always easily identified because the usual Born-Oppenheimer separation of nuclear and electronic motion does not apply. High- l states correspond to a nonpenetrating Rydberg electron, so that the molecular ion core rotates and vibrates essentially *independently* of the motion of the Rydberg electron [Hund's coupling case (d)]. However, a weak coupling of the electron to the rotating core persists, owing to the anisotropy of the molecular core, and produces a complicated fine-structure pattern. This rotational-electronic fine structure is characteristic of a given molecule, because the anisotropic field components are different for different molecular ions. The analysis is further complicated by the superposition of vibrational sequence transitions.²

In this communication we report the observation of the $n=5, l=4 \rightarrow n=4, l=3$ Rydberg-Rydberg infrared transition by high-resolution Fourier-transform spectrometry. Although this transition has previously been identified by Dressler, Jungen, and Miescher⁷ in the low-resolution emission spectrum of hot air,^{8,9} all attempts to record it under high resolution have hitherto been unsuccessful. Recent experimental progress has made it feasible to apply the technique of Fourier-transform spectrometry¹⁰ to the investigation of emission spectra from *supersonically*

expanding jets.¹¹ In this way the advantage of observing rotationally cold spectra can be combined with the high sensitivity of Fourier-transform spectrometry. Here, we apply this technique to the investigation of the $4\text{-}\mu\text{m}$ band of *cold* NO, complementing our observations on the same transition of *hot* NO gas. The cold spectrum furnishes the key to the quantitative analysis of all our observations. The conclusions of the previous Ref. 7 are fully verified by the present work.

It is difficult to produce a source which gives appreciable $5g \rightarrow 4f$ emission. Excitation of NO in a dc discharge tends to produce strong spectra of decomposition products such as N_2 , O_2 , N_2O , and atomic N I or O I. Therefore it is necessary to excite NO in a discharge which is run at high enough power so that highly excited states are populated, but which at the same time is mild enough such that the NO chemical bond is not broken. We have found it best to work with an electrodeless radiofrequency discharge, thereby avoiding problems that might arise from corrosion of the electrodes; e.g., instabilities of the source which are undesirable in Fourier-transform spectrometry. On the other hand, electrodeless discharges tend to produce rotationally hot spectra which for the high- l transitions of interest here cannot be fully resolved. The spectra presented in Fig. 1 are of this type. They have been generated in an electrodeless radiofrequency discharge through flowing nitric oxide. The pressure in the cell (~ 3 Torr) and the power of the transmitter were adjusted for maximum intensity in the 600-nm emission band of NO. A calcium fluoride lens focused the light onto the entrance iris of a Bomem D A3002 Fourier-transform spectrometer. The maximum optical path difference was 40 cm, giving an apodized resolution of 0.025 cm^{-1} . Detection was by a nitrogen-cooled InSb detector (Infrared Associates Inc.). Initially only very weak features were observed near 2500 cm^{-1} . Subsequently, after accumulation of 1000 scans during 15 h, the spectrum of Fig. 1(a) was obtained. This spectrum contains a large number of lines which belong to the $2\nu_1$

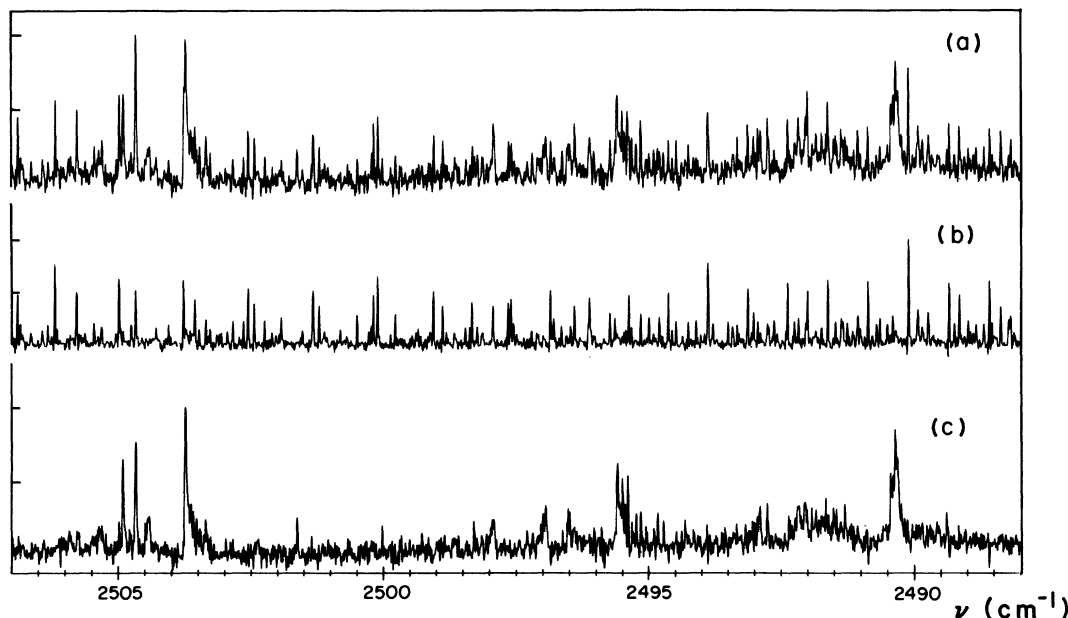


FIG. 1. (a) Emission spectrum near $4 \mu\text{m}$ of a discharge through NO gas recorded by Fourier-transform spectrometry. (b) Corresponding spectrum obtained from a discharge through N_2O . (c) Difference spectrum of (a) and (b).

and $\nu_1 + 2\nu_2$ infrared bands of N_2O . A spectrum of pure N_2O has also been recorded under similar conditions [Fig. 1(b)] and has been subtracted from the spectrum of Fig. 1(a). This procedure yielded the NO spectrum shown in Fig. 1(c). We will show below that in spite of its high resolution this spectrum is, in fact, rotationally unresolved.

The cold spectrum has been obtained by running a dc discharge in supersonically expanding He seeded with NO. A similar setup has recently been used for recording the $4f \rightarrow 3d$ transition of NO.¹¹ In order to record the $5g \rightarrow 4f$ transition it has been necessary to use highly sensitive detection. We have used a liquid nitrogen-cooled InSb detector (1DH-100/EEH-100, Cincinnati Electronics) combined with a tunable narrow-band pass interference filter, centered at $4 \mu\text{m}$ and mounted inside the detector dewar. The spectrum shown in Fig. 2 resulted after an accumulation time of 7 h. It corresponds to an apodized resolution of 0.03 cm^{-1} .

The level patterns resulting from the weak medium-range interactions between a high- l electron and a diatomic ion have previously been studied in detail.^{12,13} In a homonuclear or nearly homonuclear molecule, the main effect is due to the electrostatic quadrupole field of the core which yields a first-order splitting of each hydrogenic nl state into $l+1$ axial components. As in atoms, core polarization lowers the entire manifold of levels with respect to the hydrogenic energy, and it also contributes to the splitting. For fixed nuclei, the shifts of the Rydberg levels are approximately proportional to the square of the orbital angular momentum component Λ along the internuclear axis:

$$T_{nl\Lambda} = T_{nl,\Lambda=0} + k_{nl}\Lambda^2. \quad (1)$$

Apart from smaller contributions due to core polarization, the constant k_{nl} is proportional to the molecular

quadrupole moment Q_{zz} of the ion core. However, Eq. (1) does not produce the level pattern which is generally observed, the reason being that a nonpenetrating Rydberg electron interacts with the *rotationally averaged* rather than with the *static* core field. If the core rotation is extremely fast, the rotational axis will effectively take over as quantization axis. In this limit, and since $Q_{xx} = Q_{yy} = -\frac{1}{2}Q_{zz}$, Eq. (1) becomes replaced by

$$T_{nl\mathcal{L}} = T_{nl,\mathcal{L}=0} - \frac{1}{2}k_{nl}\mathcal{L}^2, \quad (2)$$

where \mathcal{L} is the semiclassical component of l along the *rotational axis* of the molecular core. [There is a straightforward relationship between the energies $T_{nl,\Lambda=0}$ and $T_{nl,\mathcal{L}=0}$ since the centers of gravity of the $2l+1$ states represented by the two Eqs. (1) and (2) in fact coincide.] The observed fine-structure patterns follow neither Eq. (1) nor Eq. (2) exactly. Rather, for each value of the quantum number N representing the total angular momentum apart from electron spin, $2l+1$ separate levels occur whose ordering is somewhere in between the Λ structure predicted by Eq. (1) and the \mathcal{L} structure predicted by Eq. (2) and depends on n and l as well as on the strengths of the medium-range core field components.

In quantitative calculations it is necessary to account fully for the coupling of the core angular momentum N^+ and the orbital angular momentum l . Reference 13 discusses various ways in which the calculation of the rotational-electronic structure of a pure high- l complex of levels can be set up. Each calculation requires the knowledge of the $l+1$ hypothetical fixed-nuclei electronic energies $T_{nl\Lambda}$ and the rotational core energy levels $E(N^+) = B^+N^+(N^++1) - D^+[N^+(N^++1)]^2$. In addition, the electronic dipole transition moments $d_{n''l''\Lambda''}^{n'l\Lambda}$ for the photoemission process are required. When the Rydberg electron is nonpenetrating they can be taken to be

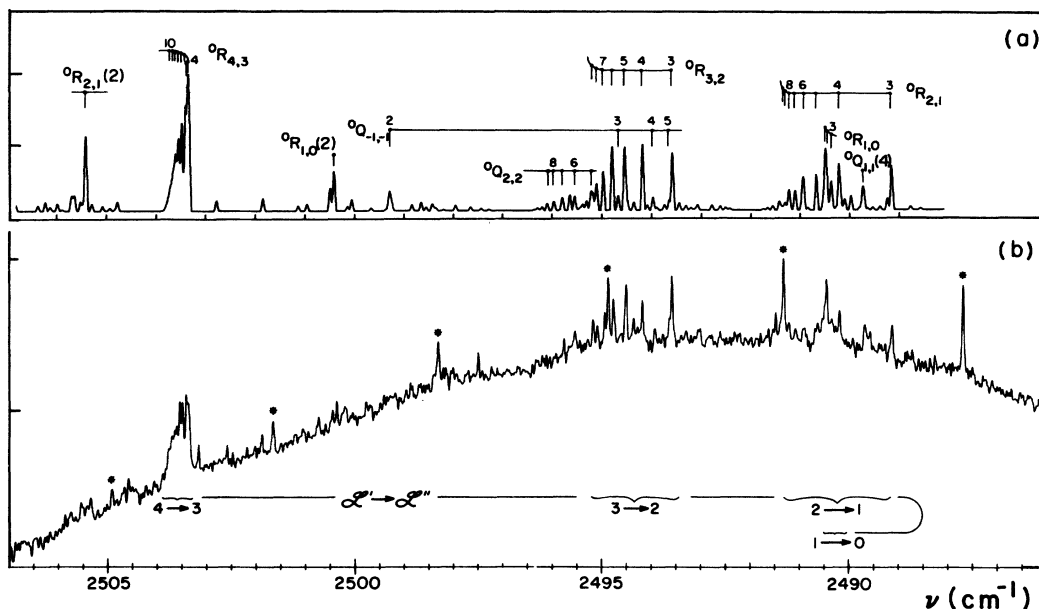


FIG. 2. The $5g \rightarrow 4f$ transition of rotationally cold NO. (a) Calculated spectrum, $T_{\text{rot}} = 70$ K. (b) Observed emission spectrum of a supersonic jet discharge. Transitions $\mathcal{L}' \rightarrow \mathcal{L}''$ are indicated. Lines belonging to the R branch of the $S^2\Sigma^+ \rightarrow M^2\Sigma^+$ transition of NO are marked by asterisks.

equal to those of the hydrogen atom.⁷ The rotational-electronic energy levels of the $4f$ state of NO as well as the purely electronic energies $T_{4f\Lambda}$ of the $4f$ state of NO and the rotational constants of NO^+ are precisely known from earlier experiments,^{11,14} so that at this stage, neglecting electron spin effects, only $T_{5g\Sigma}$ and k_{5g} remain as unknown quantities. These two parameters can be estimated on the basis of the known quadrupole moment and polarizabilities of NO^+ ($v^+ = 0$), viz., $Q_{zz} \sim 0.41$, $\alpha \sim 7.7$, and $\frac{1}{3}(\alpha_{\parallel} - \alpha_{\perp}) \sim 2.5$ a.u., quantities which have previously been extracted from the electronic Λ structure of the $4f$ complex of states.^{11,12} The evaluation was based on the use of hydrogenic radial wave functions for the high- l Rydberg electron. Using these predictions we have made a preliminary calculation of the cold spectrum. The obvious overall resemblance between the calculated and observed spectra [Fig. 2(b)] immediately led to the rotational line assignments indicated in Fig. 2. Finally, a nonlinear least-squares fit based on these assignments yielded the refined values $T_{5g\Sigma} = 70\,325.621 \pm 0.006$ and $k_{5g} = 0.3817 \pm 0.0008$ cm^{-1} . The calculated spectrum shown in Fig. 2 opposite the observed spectrum corresponds to these values. Table I contains the frequencies of the assigned $5g \rightarrow 4f$ lines and the energy levels of the $5g$ ($v=0$) complex obtained by adding the known $4f$ energies. The observed and calculated deviations are also listed; their mean is 0.009 cm^{-1} for the lines included in the fit.

The agreement of the observed and calculated spectra in Fig. 2 is convincing evidence that the $4\text{-}\mu\text{m}$ band of NO represents the $5g\text{-}4f$ ($v=0$) transition. A few lines of the $5s\sigma S^2\Sigma^+ \rightarrow 4p\sigma M^2\Sigma^+$ Rydberg-Rydberg transition have also been identified and are indicated in the figure by asterisks. Vibrational sequence transitions $5g\text{-}$

$4f$ ($v > 0$), on the other hand, are absent. The rotational lines of the $5g\text{-}4f$ ($v=0$) band are labeled $N^+ - N''$, $\Delta N_{\mathcal{L}',\mathcal{L}''}$, where $\mathcal{L} = N - N^+$ is the difference of the total and core angular momentum quantum numbers excluding electron spin. In the classical limit where $N \gg l$, \mathcal{L} can be interpreted as the projection of l along the rotational axis, as implied by Eq. (2). All the observed branches have Q form ($N^+ = N''$), reflecting the fact that the core remains in the same state during the electronic transition.

Using the parameters derived from the analysis of the cold spectrum of Fig. 2 we are now in a position to calculate the hot spectrum. We have assumed a temperature of 850 K, and we have convoluted the calculated spectrum with the experimental linewidth. The result is shown in Fig. 3. The agreement between the observed and calculated spectra is again fairly good, showing beyond a doubt that, except for the two peaks near 2505 cm^{-1} , the experimental spectrum is a pure spectrum of the $5g\text{-}4f$ ($v=0$) transition of hot NO. The calculation further shows that the observed hot spectrum is rotationally *unresolved*: despite their apparent sharpness (of the order of 0.05 cm^{-1}), the spikes seen in Fig. 3 result from accumulations of large numbers of lines associated with high core rotation. For instance, within an interval of 0.1 cm^{-1} the peak of 2503.8 cm^{-1} contains no less than 20 lines of more or less comparable intensity which arise in transitions from $\mathcal{L}' = 4$ to $\mathcal{L}'' = 3$ and correspond to N^+ values ranging from 10 to 30.

In order to reproduce these accumulations correctly in the calculations, the energy levels of the combining states must be calculated correctly to better than the experimental resolution of 0.025 cm^{-1} . The theoretical model for an unperturbed high- l complex of states reviewed in

TABLE I. Observed rotational lines of the $5g-4f(v=0)$ transition of $^{14}\text{N}^{16}\text{O}$ and term values of the $5g(v=0)$ levels relative to $X^2\Pi_{1/2}(v=0, J=0.5)$ (cm^{-1}). The observed and calculated ($o-c$) deviations are also given.

Observed line	$o-c$	$N^{+'}=N^{+''}$	N'	N''	\mathcal{L}'	\mathcal{L}''	$5g(v=0)$ term value
2489.116	0.014	2	4	3	2	1	70 341.56
2490.182	0.004	3	5	4	2	1	353.44
2490.625	0.008 ^a	4	6	5	2	1	369.25
2490.882 ^b	-0.003 ^a	5	7	6	2	1	389.03
2491.073	0.001 ^a	6	8	7	2	1	412.80
2491.202	0.002 ^a	7	9	8	2	1	440.56
2489.669 ^b	-0.008 ^a	3	4	4	1	1	352.93
2490.340	0.021 ^a	3	4	3	1	0	352.96
2490.443 ^b	-0.012	4	5	4	1	0	369.08
2490.443 ^b	-0.035 ^a	5	6	5	1	0	389.02
2490.443 ^b	-0.013 ^a	6	7	6	1	0	412.92
2493.566	-0.002	1	4	3	3	2	333.92
2494.162	0.004	2	5	4	3	2	341.23
2494.490	-0.003	3	6	5	3	2	352.81
2494.746	-0.006	4	7	6	3	2	368.48
2494.916	-0.013	5	8	7	3	2	388.20
2495.069	0.008	6	9	8	3	2	411.95
2495.154	0.032 ^a	3	5	5	2	2	353.47
2495.521	0.018 ^a	4	6	6	2	2	369.26
2495.740	-0.006 ^a	5	7	7	2	2	389.02
2503.358 ^b	-0.034 ^a	0	4	3	4	3	327.76
2503.358 ^b	0.036 ^a	1	5	4	4	3	331.30
2503.398	-0.018 ^a	2	6	5	4	3	338.96
2503.477	0.011	3	7	6	4	3	350.78
2503.528	-0.008	4	8	7	4	3	366.57
2503.589	0.002	5	9	8	4	3	386.39
2503.630	0.001	6	10	9	4	3	410.19
2503.688	-0.007 ^a	7	11	10	4	3	438.01

^aLine not included in the fitting.

^bBlended line.

Ref. 13 does not quite achieve this for the $4f$ state, since these levels have been reproduced in Ref. 11 with a mean deviation of 0.04 cm^{-1} only. The small deviations arise because the assumption of nonpenetration is not quite strictly true for the $l=3$ electron, and as a consequence weak interactions occur with states outside the $l=3$ man-

ifold. A discussion of these perturbations in NO may be found in Ref. 11, and a quantitative interpretation of similar perturbations in the $4f$ states of He_2 in Ref. 13. In the calculation of the hot temperature spectrum, we have therefore replaced the calculated $4f$ levels by the observed energies whenever this was possible. By con-

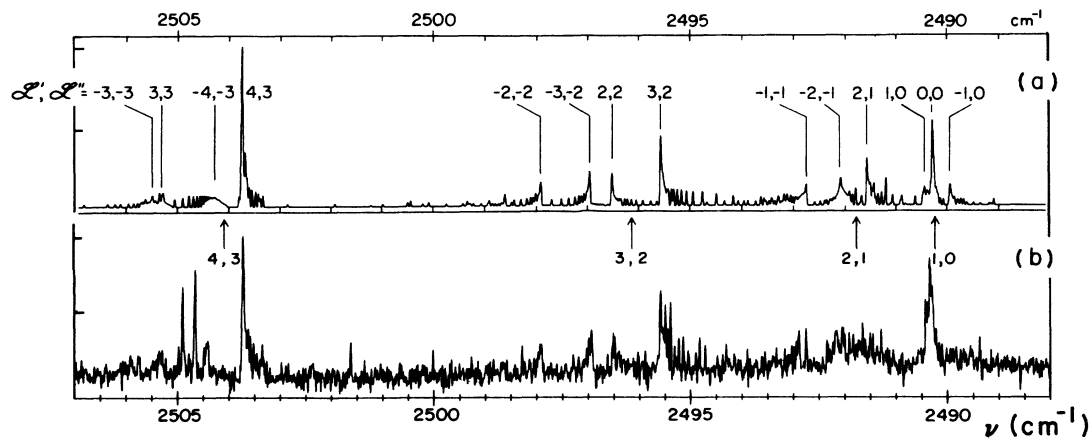


FIG. 3. The $5g \rightarrow 4f$ transition of rotationally hot NO. (a) Calculated spectrum, $T_{\text{rot}} = 850 \text{ K}$. (b) The observed $4\text{-}\mu\text{m}$ band of hot NO.

trast, the resulting good agreement of the calculated with the observed spectra confirms that the theoretical model is adequate for the $5g$ states and predicts the high rotational levels very accurately. Specifically, we conclude that the quadratic relationship of Eq. (1) represents the hypothetical fixed-nuclei electronic energies of the $5g(v=0)$ complex with high accuracy. Note that this is not the case for the $4f$ states. Although the four electronic states forming the $4f$ complex are spaced more or less according to Λ^2 (corresponding to $k_{4f} \sim 3.6 \text{ cm}^{-1}$), there are deviations of the order of 1 cm^{-1} , and therefore the four values T_A are more appropriately treated as independent quantities.¹²

The $4\text{-}\mu\text{m}$ band of hot NO shown in Fig. 3 represents a new type of molecular band spectrum. Earlier work⁷ has anticipated the existence of such spectra; here, we present the first highly resolved experimental example. This band type is characterized by the formation of sharp spikes which correspond to specific values of \mathcal{L}' and \mathcal{L}'' . From atomic one-electron theory, and interpreting \mathcal{L} as the projection of l onto the rotational axis, we expect the transitions $\mathcal{L} \rightarrow \mathcal{L}-1$ to dominate. The $\mathcal{L}' \rightarrow \mathcal{L}'' = 4 \rightarrow 3$, $3 \rightarrow 2$, $2 \rightarrow 1$, and $1 \rightarrow 0$ transition energies calculated ac-

ording to Eq. (2) are indicated in the figure by arrows: it can be seen that, indeed, they predict correctly the main features of the $4\text{-}\mu\text{m}$ band which, therefore, represents an \mathcal{L} structure. In the same vein we may interpret the strong $\mathcal{L}'=4 \rightarrow \mathcal{L}''=3$ peak as a transition between circular states¹⁵ because \mathcal{L} equals $n-1$ in the combining levels. Circular states are nowadays common objects of study in atoms.¹⁶ While in atomic spectroscopy the splitting of the l manifold results from the application of an external Stark field, it is brought about in the molecule by the anisotropic components of the rapidly rotating molecular ion core. Note, finally, that the formation of spikes is much less pronounced in the cold spectrum of Fig. 2 than in the hot spectrum of Fig. 3. The former spectrum corresponds to low values of N , for which the quantum number difference $\mathcal{L} = N - N^+$ cannot be identified with the projection of l along the rotation axis. This spectrum is more nearly similar to the $5g \rightarrow 4f$ transition of H_2 .²

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