Cavity ringdown spectrum of the forbidden $\tilde{A}^2E'' \leftarrow \tilde{X}^2A'_2$ transition of NO$_3$: Evidence for static Jahn–Teller distortion in the $\tilde{A}$ state

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The Jahn–Teller effect in the first two excited states of the nitrate radical NO$_3$ has yet to be experimentally elucidated. In this paper, direct evidence of strong Jahn–Teller interactions in the $\tilde{A}$ state is presented from the first complete absorption spectrum of the $\tilde{A}^2E'' \leftarrow \tilde{X}^2A'_2$ transition of NO$_3$ in the gas phase in the region 5900–9000 cm$^{-1}$, at moderate resolution (0.15 cm$^{-1}$). The observed spectrum is consistent with Herzberg–Teller selection rules, and reveals strong linear and quadratic Jahn–Teller interactions in the $\tilde{A}$ state. Several of the vibronic bands have been tentatively assigned, including $\nu_2$, $\nu_3$, an irregular progression in $\nu_4$, and combination bands involving $\nu_1$. Our assignments are consistent with the previous works of Weaver et al. [A. Weaver, D. W. Arnold, S. E. Bradforth, and D. M. Neumark, J. Chem. Phys. 94, 1740 (1991)] and Hirota et al. [E. Hirota, T. Ishiwata, K. Kawaguchi, M. Fujitake, N. Ohashi, and I. Tanaka, J. Phys. Chem. 107, 2829 (1997)]. The band origin is not observed, in accord with the selection rules, but is determined to be $T_0=7064\text{ cm}^{-1}$ from the observation of the $4^4_1$ hot band at 6695.7 cm$^{-1}$. Rotational contour analysis of this band indicates that the upper state is an asymmetric rotor, establishing that NO$_3$ undergoes static Jahn–Teller distortion in the ground vibrational level of the $\tilde{A}$ state. © 2005 American Institute of Physics. [DOI: 10.1063/1.1897364]

I. INTRODUCTION

As an open-shell molecule with $D_{3h}$ symmetry, the nitrate radical NO$_3$ exhibits the Jahn–Teller effect in its degenerate electronic states. There have been many detailed theoretical studies of the vibronic interactions in the ground and the first two excited states of NO$_3$, and this radical has become a model system for studying the Jahn–Teller and pseudo-Jahn–Teller effects. However, despite numerous spectroscopic studies, there is little direct experimental data on the Jahn–Teller effect in gas phase NO$_3$.

Walsh$^1$ correctly predicted the electronic configuration of the ground state, $(4e')^4(1e'')^4(1a_2^2)$, and proposed that the three orbitals were all close in energy. Single excitations from the $(1e'')$ and $(4e')$ orbitals to the $(1a_2^2)$ orbital produce the first two excited states, $\tilde{A}^2E''$ and $\tilde{B}^2E'$, respectively. The geometry of the ground $\tilde{X}^2A'_2$ state was the subject of some controversy, and only recently have experiment and theory confirmed that it has a planar $D_{3h}$ geometry.$^2$–$^4$ The two excited states must exhibit the Jahn–Teller effect, but neither excited state is well characterized. A quantitative description of the Jahn–Teller effect in NO$_3$ is complicated because all three levels interact via vibronic coupling.$^5$ and NO$_3$ has two Jahn–Teller active modes, the degenerate asymmetric stretch $\nu_3$ and bend $\nu_4$ vibrations, rendering it a multimode problem.

The higher $\tilde{B} \leftarrow \tilde{X}$ transition, first observed in the gas phase by Jones and Wulf,$^6$ gives rise to broad, relatively unstructured absorption bands between 680 and 450 nm. The transition is strong [$\sigma$ (662 nm)=2.2×10$^{-17}$ cm$^2$] and has been studied extensively,$^{10}$ but the upper vibronic levels have only been tentatively assigned,$^{11}$ and even jet cooling has not helped.$^{12}$ The spectral complexity, line broadening, and anomalous fluorescence decay all suggest strong vibronic coupling.

There have been few experimental studies of the first electronic state $\tilde{A}^2E''$ of NO$_3$. The transition $\tilde{A} \leftarrow \tilde{X}$ is forbidden, but it is vibronically allowed by the Herzberg–Teller effect and therefore weak. Weaver et al.$^5$ first observed the $\tilde{A}$ state by anion photoelectron spectroscopy (PES) of NO$_3$ and found $T_0(\tilde{A})=7000\pm110$ cm$^{-1}$. They observed a series of peaks which they fit to mixed progressions of two harmonic modes, $541\pm8$ and $804\pm4$ cm$^{-1}$. They tentatively assigned these modes to $\nu_3$ and $\nu_4$, respectively. In a Fourier transform infrared (FTIR) spectrum of NO$_3$,$^{15}$ Kawaguchi et al.$^7$ discovered two near infrared (NIR) absorption bands at 7602 and 7744 cm$^{-1}$, which they assigned to the $4^4_0$ and $2^2_0$ transitions, though only band positions and type were listed. Hirota et al.$^8$ employed diode laser spectroscopy to obtain a rotationally resolved spectrum of the 7602-cm$^{-1}$ band.$^{16}$ They fit the spectrum to a parallel band of a $D_{3h}$ symmetric top, and assigned it to a transition of the $2^2E''$ vibronic component of the $\nu_3$ mode of the $2^2E''$ state. The upper state could be described with a symmetric-top Hamiltonian with a diagonal spin-rotation term, with few perturbations. These results sug-
suggest that NO₃ in the A state is symmetric, i.e., it exhibits the dynamic Jahn–Teller effect with weak vibronic interactions.

This result appears to disagree with a high-level ab initio study of the excited states of NO₃ by Eisfeld and Morokuma. They optimized the structures of NO₃ in the A and B states at the complete active space self-consistent field (CASSCF) and multi-reference single and double excitation configuration interaction (MR-SDCI) levels of theory. They found that the A state undergoes significant Jahn–Teller distortion. NO₃ in the A state is localized in three C₂ᵥ minima with B₂ symmetry lying ≈2000 cm⁻¹ below the conical intersection. The transition states between the minima were 800–1000 cm⁻¹ higher in energy. Such a large stabilization energy and high barrier to pseudorotation indicate strong linear and quadratic Jahn–Teller effects in the A state.

Our experimental knowledge of the A state is thus incomplete and at odds with theoretical predictions. Furthermore, the experimental results to date shed little light on the Jahn–Teller states, due to the large and erratic variations in band spacings and even rotational structure arising from the vibronic perturbations. Rather, the full spectrum must be acquired and, even then, great care must be taken in assigning vibronic bands. For NO₃, a comprehensive absorption spectrum of the A state can provide definitive insights into the nature of the Jahn–Teller effect in this important molecule.

In this work, we exploit the sensitivity of the cavity ringdown method to detect the forbidden ÆE′ ← ÆA′₂ transition of NO₃ in the range of 5900–9000 cm⁻¹.

II. EXPERIMENT

The NIR absorption spectrum of NO₃ was recorded by pulsed cavity ringdown spectroscopy of room-temperature NO₃ in a flow cell in an apparatus similar to the one used by Pushkarsky et al. Tunable NIR radiation was generated by stimulated Raman scattering in hydrogen. The output of a YAG-pumped dye laser (Continuum TDL51 and NY60) was directed through a 2-m-long multipass Raman cell containing 6–9 atm of H₂. The NIR pulse (0.5–1 mJ) was generated as the second Stokes of the dye beam (5–20 mJ, ≈0.15 cm⁻¹ linewidth) in three passes, and then filtered and slightly focused into the ringdown cell.

Reactant gases were flowed through a 40-cm-long, 1.27-cm-diameter Pyrex cell. Two high reflectivity mirrors formed the optical cavity, which was coaxial with the gas cell, and were separated from the reaction region by 20-cm-long purge volumes. Three sets of mirrors were used: Newport 1-m-ROC (radius of curvature) mirrors (5900–7000 and 7000–8000 cm⁻¹) and Los Gatos Research 6-m-ROC mirrors (7900–8950 cm⁻¹).

The NIR radiation exiting the cavity was tightly focused onto a 1-mm-diameter extended InGaAs photodiode (Hamamatsu). The photodiode signal was amplified and digitized by a 12-bit transient digitizer (Gage Compuscope 1012). Twenty ringdown traces were typically averaged and then fit to a single-exponential function using the NL2SOL algorithm.²¹

NO₃ was produced in a reaction of ozone with N₂O₅. A 1% mixture of O₃ in O₂ passed through a trap containing solid N₂O₅ held at −20 °C, and was then flowed into the reaction cell. Nitrogen was flowed through the purge volumes to protect the mirrors. The gas in the cell, at a pressure of 45–50 Torr, was flowed through at a rate of 45 sccm (sccm denotes cubic centimeter per minute at STP) (4.5-s residence time). To eliminate absorption by N₂O₅ and residual water, a background scan was taken with the ozonizer off after every run and subtracted from the spectrum. NO₃ was also produced by photolysis of CIONO₂ and N₂O₅, to confirm the identity of the observed bands.

The NO₃ concentration was measured between scans by direct absorption at 661.5 nm using a diode laser. The diode laser beam was collinear with the NIR radiation and...
detected with the same photodiode. Single pass absorbances were typically 5%–10%, yielding \( \text{NO}_3 = 8 \times 10^{13} \pm 2 \times 10^{14} \) mol/cm\(^3\).

III. RESULTS

The spectrum of \( \text{NO}_3 \) is shown in Fig. 1. Scans with different laser dyes were scaled by matching the intensities of the bands present in overlapping regions, or by scaling with the measured \( \text{NO}_3 \) concentration. We detected a series of absorption bands in the 5900–9000 cm\(^{-1}\) range, though absorption by nitric acid prevented the detection between 6900 and 7000 cm\(^{-1}\). Using chemistry, background subtraction, and contour analysis, we attributed all of these bands to \( \text{NO}_3 \). Only three weak bands were found between 5900 and 7500 cm\(^{-1}\), peaked near 6700 and 7230 cm\(^{-1}\). Above 7500 cm\(^{-1}\), we observed a series of bands (including the two bands reported previously) which became increasingly congested, especially above 8700 cm\(^{-1}\). There are no obvious spin-orbit doublets, indicating that spin-orbit coupling must be largely quenched.

Most of the vibronic bands had sharp \( R \)-branch bandheads and widths of \( \approx 50 \) cm\(^{-1}\), though some band shapes were obscured in the congested regions. Simulations of rotational contours with the \( \text{NO}_3 \) constants obtained by Hirota et al. show that parallel and perpendicular bands are easily distinguished: both have sharp \( R \)-branch bandheads, but perpendicular bands have a sharper bandhead and no gap between the \( P \) and \( R \) branches. The majority of the well-resolved bands are perpendicular bands, but five are clearly parallel bands; only the 8287(3)-cm\(^{-1}\) band does not resemble the simulated contours. Band centers are estimated from the contour analysis.

IV. ANALYSIS

The forbidden \( \tilde{A} \rightarrow \tilde{X} \) transition becomes allowed via vibronic coupling. Only vibronic states with symmetries of \( \Gamma_{v^e} = A''_1 \) or \( E' \), for parallel and perpendicular bands, respectively, can be excited by transitions from the \( 0_0 \) state. The umbrella mode \( \nu_4 \) and its odd quanta have \( \Gamma_{v^e} = A''_2 \otimes E'' = E' \) symmetry and will give rise to perpendicular bands. The degenerate \( e' \) modes \( \nu_1 \) and \( \nu_2 \) split into three vibronic states \( e' \otimes E'' = A''_1 \otimes A''_2 \otimes E'' \) by vibronic coupling. Only the \( A''_2 \) component will be observed, as a parallel band, in the absence of spin-orbit coupling. The overtones and combination bands of these modes will split into a larger number of vibronic states of the same symmetries; most components will be forbidden. The symmetric stretch \( \nu_1 \) is not allowed, and can be observed only in combination with other allowed modes.

The \( \nu_1 \) and \( \nu_4 \) modes are Jahn–Teller active and even small Jahn–Teller coupling can split the vibronic levels and lead to irregular spacings. For these modes, \( \nu \) is no longer a good quantum number and is used here to indicate the state with the largest contribution to the eigenfunction of the Jahn–Teller Hamiltonian. The non-Jahn–Teller active modes, however, should behave normally and form regular progressions. Perturbations due to the Jahn–Teller effect make assignments tenuous; in this paper, we therefore assign only the more prominent features.

The \( 0_0 \) band is vibronically forbidden, though a weak absorption was indeed detected between 7040 and 7080 cm\(^{-1}\) near the expected origin, \( \nu_0 = 7060 \) cm\(^{-1}\). However, due to the low signal-to-noise ratio (S/N \( \approx 10 \)) and interference of the water lines, we could not assign this band unambiguously. A weak parallel transition was observed at 6695.7 cm\(^{-1}\) (Fig. 2), \( \approx 365 \) cm\(^{-1}\) below the expected origin. The \( \nu_4^0 \) mode in the ground state is 368 cm\(^{-1}\) from laser-induced fluorescence (LIF) measurements,\(^{12}\) and has a 298-K Boltzmann factor of 0.34, consistent with the observed intensity. We therefore assign this band to the \( 4_1^0 \) hot band transition.

This hot band allows us to determine with more confidence the position of the origin. We estimate \( T_{00}(\tilde{A}) = 7064 \) cm\(^{-1}\). The accuracy is limited by the uncertainty in determining the origin of the LIF band, but this is not known. However, the current value is certainly more accurate than the previously reported value of 7061 \( \pm 8 \) cm\(^{-1}\), which was based on the \( \nu_4 \) frequency of 540 cm\(^{-1}\) in the PES spectrum. The \( \pm 8 \) cm\(^{-1}\) uncertainty comes from fitting the PES peaks to the harmonic progressions.\(^5\) The actual uncertainty in the previous value is likely to be much larger, because the overtone and combination band frequencies of a Jahn–Teller active mode will result in shifts of tens of wavenumbers.

We assign a series of similar parallel bands at 7602(1), 8121(1), and 8668(1) cm\(^{-1}\) to a progression in \( \nu_4 \). Specifically, these are the \( |j = 3/2, a''_1 \rangle \) states of the \( n\nu_4 e' \otimes E'' \) vibronic manifolds. Here \( j \) is a first order Jahn–Teller quantum

![Fig. 2. Spectrum of the 4_1^0 hot band. (a) Simulation-symmetric top, (b) simulation-asymmetric top, and (c) experiment. The * represent positions of strong water lines which may give residual peaks even after background subtraction.](image-url)
number.\textsuperscript{16} This confirms the assignment of the 7602.545-cm\(^{-1}\) band by Hirota \textit{et al.} The irregular spacings, 539, 519(1), and 547(1) cm\(^{-1}\), are evidence of the Jahn–Teller coupling. While it is conceivable that the weak band at 7230 cm\(^{-1}\) could be \(4_{1}^{0}\), its intensity and band shape differ from the others in the progression.

The 7742(1)-cm\(^{-1}\) band is the first and strongest of a series of perpendicular bands. Perpendicular bands must involve the umbrella mode, \(\nu_{2}\). The prominence of these bands is expected, because this mode is responsible for the intensity borrowing by pseudo-Jahn–Teller coupling from the strong \(\tilde{B} \rightarrow \tilde{X}\) transition. We assign the 7742-cm\(^{-1}\) band to the fundamental of \(\nu_{2}\), in agreement with the study of Kawamura \textit{et al.}\textsuperscript{15} giving \(\nu_{2}=678\) cm\(^{-1}\) in the upper state.

The other perpendicular bands are combination bands with \(\nu_{1}\) or its overtones with odd \(\nu_{2}\). The strong perpendicular band at 8527-cm\(^{-1}\) band lies 785 cm\(^{-1}\) to the blue, which is close to the predicted\textsuperscript{17} frequency for the symmetric stretch, \(\nu_{1}=800\) cm\(^{-1}\). We assign it to the \(\nu_{1} + \nu_{2}\) combination band. This value falls between the frequency of the first peak (750 cm\(^{-1}\)) in the anion PES spectrum\textsuperscript{5} and the (less reliable) value of 804 cm\(^{-1}\) obtained from the harmonic fit of the \(\nu_{1}\) progression.

Other possible combination bands with \(\nu_{1}\) include the 8365(3)- and 8900(3)-cm\(^{-1}\) bands, which we tentatively assign to \(1_{2}^{10} + 1_{2}^{12}\) and \(1_{2}^{14} + 1_{2}^{10}\). These bands overlap with adjacent bands, partially obscuring their contours. The values of \(\nu_{1}\) in these combination bands would be 763(3) and 779(3) cm\(^{-1}\), respectively. The differences in apparent \(\nu_{1}\) frequencies are likely due to the intrinsic vibrational anharmonicity and/or to the bilinear vibronic coupling between the \(\nu_{1}\) and \(\nu_{2}\) modes.

We simulated the rotational contours of several vibronic bands in detail to find evidence of the static Jahn–Teller distortion in NO\(_{3}\). Static distortion leads to the asymmetry in the averaged structure. We employed \textsc{spcat} (Ref. 22) and \textsc{asyrot} (Ref. 23) programs to model the rotational contours using symmetric- and asymmetric-top Hamiltonians, respectively. Our simulations included the known centrifugal constants for the ground state \(0\)\(_{0}\) and the \(1\)\(_{1}\) state, but ignored spin-rotation and Coriolis couplings. Because the rotational constants of the \(1\)\(_{1}\) state are not known, we used the ground \(0\)\(_{0}\) state constants for the lower state of the 6696-cm\(^{-1}\) band (we explicitly assume that the structure retains \(D_{3h}\) symmetry in the hot lower level, i.e., with one quantum in \(\nu_{4}\) of the \(\tilde{X}\) state).

The observed profiles of the bands in the \(n\nu_{4}\) progression were simulated well using the symmetric top Hamiltonian with the rotational constants of Hirota \textit{et al.}\textsuperscript{16} For the \(4\)\(_{1}\) and \(4\)\(_{3}\) bands, the upper-state constants had to be scaled by 0.987 and 0.975, to achieve better agreement, indicating an overall increase in the structure in these levels.

The symmetric-top model, however, failed for the \(4\)\(_{1}\) hot band and the \(2\)\(_{1}\) band. The results of the simulations using both symmetric- and asymmetric-top Hamiltonians for the \(4\)\(_{1}\) band are shown in Fig. 2. The symmetric-top model was not able to predict the width of the bandhead of the \(4\)\(_{1}\) band nor the blue shoulder of the \(2\)\(_{1}\) band. Varying the rotational constant \(B'\) of the upper state with locked planar symmetric-top relationship \(A'=B'=C'/2\) only slightly shifted the position of the bandhead without affecting the overall shape of the band. We found that it was necessary to break the \(A'=B'\) symmetry to obtain qualitative agreement with the experiment. The experimental contours of the \(4\)\(_{1}\) and \(2\)\(_{1}\) bands were best simulated with the asymmetric-top Hamiltonian, as a c-type(\(\parallel\)) band with \(\kappa'=0.59\) and as a b-type(\(\perp\)) band with \(\kappa'=0.83\), respectively.

The strongest band, at 8287(3) cm\(^{-1}\), has an unusual contour that can be simulated only if \(\kappa'=0.32\), i.e., the upper-state geometry is more distorted than in the \(0\)\(_{0}\) state. The band is a c-type(\(\parallel\)) transition and we tentatively assign it to \(3\)\(_{0}\), yielding \(\nu_{4}=1223\) cm\(^{-1}\). This assignment must be considered tenuous, given the anomalous band shape and large discrepancy of the band position with theoretical predictions.

\section{V. Discussion}

We find clear evidence of a relatively strong Jahn–Teller effect in the \(\tilde{A}\) state of NO\(_{3}\). The \(0\)\(_{0}\) level undergoes static Jahn–Teller distortion, as do the vibrationally nondegenerate \(2\)\(_{1}\) and its combination levels. Both of the Jahn–Teller active modes, \(\nu_{3}\) and \(\nu_{4}\), appear to be highly perturbed. The absence of apparent spin-orbit doublets is also indicative of relatively strong linear and quadratic Jahn–Teller couplings, which would largely quench spin-orbit coupling (<150 cm\(^{-1}\)).

Previous experimental and theoretical results give a fragmented and somewhat contradictory picture of the Jahn–Teller effect in the \(\tilde{A}\) state of NO\(_{3}\). Our results are consistent with these earlier studies, but provide a more complete picture and resolve the apparent discrepancy between theory and experiment.

The current results agree with predictions of a strong Jahn–Teller effect by Eisfeld and Morokuma\textsuperscript{17} and by Stanton.\textsuperscript{24} The observation of a distorted structure for the vibrationally nondegenerate levels of the \(\tilde{A}\) state supports the \textit{ab initio} results of Eisfeld and Morokuma and of Stanton. In MR-SDCI calculations, Eisfeld and Morokuma\textsuperscript{17} predicted a distorted \(C_{2v}\) geometry in a state of \(2\)\(_{1}\) symmetry with \(\kappa=0.88\). The vibrational frequencies observed for the nondegenerate modes agree fairly well with the MR-SDCI harmonic values (\(\nu_{1}=731\) cm\(^{-1}\) and \(\nu_{2}=802\) cm\(^{-1}\)), but those of the degenerate Jahn–Teller active modes deviate significantly from predictions [\(\nu_{3}(b_{2})=1754\) cm\(^{-1}\) and \(\nu_{4}(b_{2})=271\) cm\(^{-1}\)]. Surprisingly, the state-averaged CASSCF frequencies (800, 684, 1602, and 553 cm\(^{-1}\)) are closer for all but \(\nu_{4}\). Stanton’s equation of motion ionization potential-coupled cluster with singles and doubles and perturbative triples/triple zeta basis set with double polarization functions (EOMIP-CCSD(T)/TZ2P) calculation\textsuperscript{24} predicts a similar distorted \(\tilde{A}\) state minimum; the predicted frequencies for \(\nu_{3}(b_{2})\) and \(\nu_{4}(b_{2})\), are 1570 and 588 cm\(^{-1}\), respectively, in better agreement with experiment.

However, our results also confirm the findings of Hirota \textit{et al}. whose full rotational analysis demonstrated that the \(a_{1}\)\(_{1}\) state of \(4\)\(_{1}\) has a symmetric \(D_{3h}\) structure. We conclude that
the barrier for pseudorotation must lie at or below the 41 vibronic level, \( E < 800-1000 \ \text{cm}^{-1} \).

The behavior of the \( \nu_3 \) mode is at first glance puzzling. In the independent mode approximation, the symmetric structure of the \( \nu_4 \) band would suggest that \( \nu_3 \) has a small linear Jahn–Teller effect. The asymmetry in the 31 state is due to \( \tilde{A} \) and we expect that the \( \nu_3 \) mode to deviate so significantly. The increased distortion suggests a dynamical localization, with barrier crossing inhibited upon excitation of \( \nu_3 \) by the need for vibrational exchange. It may be that the bilinear or higher-order coupling of the symmetric mode \( \nu_3 \) with the Jahn–Teller active modes must be explicitly included.

A complete quantitative description of the Jahn–Teller effect requires detailed modeling of the observed bands, assisted by \textit{ab initio} estimates of the vibronic coupling terms. Thus, the current assignments must be considered somewhat tentative, given the pitfalls in assigning spectra in the presence of strong vibronic coupling.\(^\text{18}\) However, this experiment reveals that a wealth of spectroscopic data waits to be mined, and we expect that the \( \tilde{A} \) state of NO\(_3\) will become an important quantitative test of models of the Jahn–Teller effect. A more detailed study, including higher-resolution spectra, new \textit{ab initio} results, and shorter-wavelength scans, is underway.

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\(^{24}\) J. F. Stanton (private communication).