

Observation of the $\tilde{A}(^2B_2)$ and $\tilde{C}(^2A_2)$ states of NO_2 by negative ion photoelectron spectroscopy of NO_2^-

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This Communication describes a study of the electronically excited $\tilde{A}(^2B_2)$ and $\tilde{C}(^2A_2)$ states of NO_2 by photoelectron spectroscopy of NO_2^- . NO_2 has been extensively studied via optical spectroscopy,^{1,2} but negative ion photoelectron spectroscopy offers several advantages as a probe of the excited states. For example, the calculated $\tilde{A}(^2B_2)$ state geometry ($r_{\text{NO}} = 1.26 \text{ \AA}$, $\theta_{\text{ONO}} = 102^\circ$)³ differs greatly from the experimentally determined equilibrium geometry of the $\tilde{X}(^2A_1)$ ground state (1.19 \AA , 133.9°).⁴ Because of this large geometry change, the $\tilde{A} \leftarrow \tilde{X}$ band, which comprises much of the near infrared and visible absorption spectrum of NO_2 , is dominated by transitions to highly excited (and perturbed) vibrational levels of the \tilde{A} state. Transitions to the lowest vibrational levels are not observed because of poor Franck-Condon overlap. The experimentally determined geometry of NO_2^- (1.25 \AA , 117.5°)⁵ is much closer to the \tilde{A} state geometry, and we observe transitions to lower, previously unobserved vibrational levels of the \tilde{A} state. This allows us to estimate the \tilde{A} state origin directly from our experimental data. In addition, although the $\tilde{C}(^2A_2) \leftarrow \tilde{X}(^2A_1)$ one-photon transition is electric dipole forbidden, the \tilde{C} state is accessible via a one-electron photodetachment transition from NO_2^- . Our results represent the first direct observation of the "dark" $\tilde{C}(^2A_2)$ state.

The photoelectron spectrometer used for these experiments will be described elsewhere.⁶ Important features include a pulsed, jet-cooled beam of NO_2^- , time-of-flight mass selection of the ion, and photodetachment of the selected ion using the third, fourth or fifth harmonic (355, 266, and 213 nm, respectively) of a pulsed Nd:YAG laser. The electron kinetic energy distribution is determined by time of flight. The instrumental resolution is 8 meV at 0.65 eV electron kinetic energy, and degrades as $E^{3/2}$ at higher energy.

Ervin *et al.*⁵ recently obtained the photoelectron spectrum of NO_2^- using the 351 nm (3.532 eV) line of an argon ion laser. Our spectrum at 355 nm (not shown) reproduces their results. At this energy, only the $\tilde{X}(^2A_1)$ state of NO_2 is accessible. Comparison of our results to those of Ervin *et al.* shows that hot band contributions to our spectrum (transitions from excited vibrational levels of NO_2^-) are negligible. At the origin of the \tilde{X} state progression Ervin's resolution is better than ours (9 meV vs 21 meV), so we have used their electron affinity of $2.273 \pm 0.005 \text{ eV}$ in our calculations of excited state term values.

The 266 nm (4.660 eV) spectrum in Fig. 1(A) shows two full bands and the beginning of a third; the 213 nm (5.825 eV) spectrum in Fig. 1(B) shows three distinct bands. The improved resolution at lower electron energy is evident in these spectra. The three bands are assigned to the \tilde{X} , \tilde{A} , and \tilde{C} states of NO_2 , based on the calculated term

values.³ [The $\tilde{B}(^2B_1)$ state is not accessible by a one-electron transition from NO_2^- .]

As a first approximation, we have simulated the vibrational structure in the \tilde{A} and \tilde{C} bands using experimental values of the NO_2^- geometry and vibrational frequencies,⁵ and *ab initio* values for the NO_2 excited state properties.³ The peaks in the $\tilde{A}(^2B_2)$ band are approximately 750 cm^{-1} apart and are predominantly due to a progression in the bending mode, for which the calculated frequency³ is 739 cm^{-1} . However, the symmetric stretch frequency is predicted to be almost exactly twice that of the bend,³ and combination bands are superimposed on the more intense bending

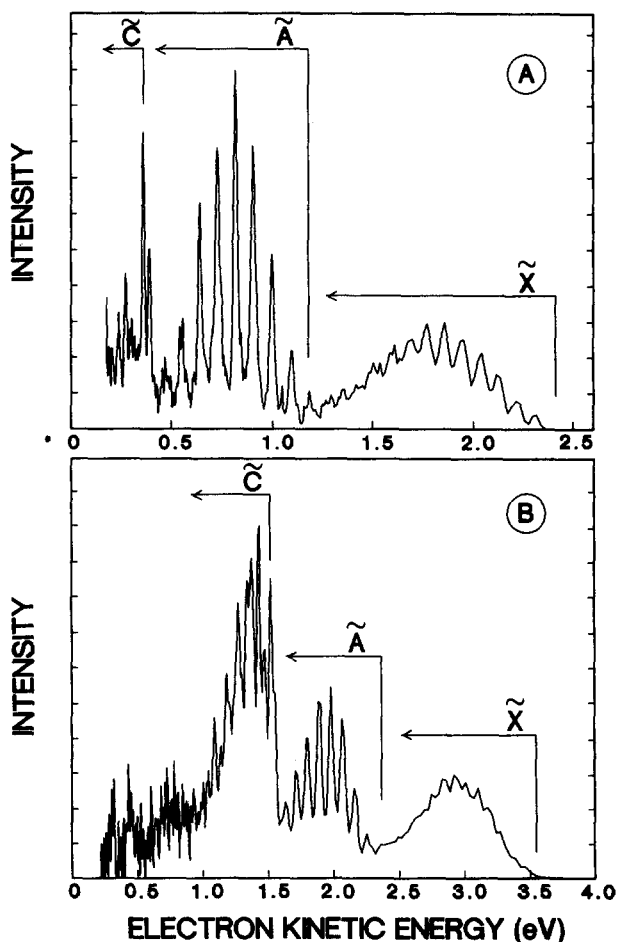


FIG. 1. Photoelectron spectra of NO_2^- . (A) 266 nm (4.660 eV); (B) 213 nm (5.825 eV). The $\tilde{X}(^2A_1)$, $\tilde{A}(^2B_2)$, and $\tilde{C}(^2A_2)$ bands are marked. The data was convoluted with 6 meV Gaussian peak envelopes, and smoothed background signal was subtracted from the 213 nm spectrum. The laser was polarized perpendicular to the electron detection direction.

progression. Antisymmetric stretch progressions are not expected to appear in any of these bands.⁵

The first peak that clearly belongs to the \tilde{A} state is at 1.183 eV electron energy in the 266 nm spectrum. The electron kinetic energy is $E = h\nu - EA - E_v - T_0$, where $h\nu$ is the laser photon energy, EA is the electron affinity of NO_2 , E_v is the vibrational energy above zero point, and T_0 is the term value for the electronic state, including zero-point energy. (We assume that the ions are rotationally cold and that the rotational energy contribution is negligible.) Using $h\nu = 4.660$ eV, $EA = 2.273$, $E_v = 0$, and $E = 1.183$, we obtain 1.204 ± 0.010 eV as an upper limit to T_0 for the \tilde{A} state. Until we analyze the spectrum completely, we cannot be sure that the origin of the \tilde{A} state band is not obscured by the end of the \tilde{X} state band, and can only assign an upper limit to T_0 . Our value agrees well with the prediction of Gillespie *et al.*³ and the extrapolated experimental value of Merer and Hallin.⁷

At the lowest electron energies in Fig. 1(A), the $\tilde{A}(^2B_2)$ progression overlaps the start of the $\tilde{C}(^2A_2)$ band. The full $\tilde{C}(^2A_2)$ band appears in the 213 nm spectrum [Fig. 1(B)]. Our analysis indicates that both the bend and symmetric stretch are active. The best match between simulated and experimental spectra is obtained by assigning the peak at 0.359 eV in Fig. 1(A) to the \tilde{C} state band origin. [This occurs at 1.516 eV in Fig. 1(B).] This yields $T_0 = 2.028 \pm 0.009$ eV for the $\tilde{C}(^2A_2)$ state, which is within the estimated error of the theoretical prediction of 1.84 ± 0.3 eV.³ The experimental \tilde{C} state progression is more extended than the simulated progression, which suggests that the bond angle in this state is smaller than the *ab initio* value of 110° .³

In conclusion, we have observed the dark $\tilde{C}(^2A_2)$ state of NO_2 for the first time and have directly measured an upper bound to T_0 for the \tilde{A} state. Our preliminary analysis indicates that the *ab initio* calculations of Gillespie *et al.*³

provide reasonable estimates of the geometries, vibrational frequencies, and term values of the \tilde{A} and \tilde{C} states. A more comprehensive analysis of our data (in progress⁸) will provide more accurate values of these properties.

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NOTES

Why separable vibrational modes dominate spectra

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Overtone spectra of many molecules, particularly hydrides, show strong, fairly isolated features which stand out above a rather weak background.¹⁻⁶ Often, these features sharpen for higher overtones. It is assumed increasingly frequently, and sometimes demonstrated, that these are "local mode" transitions. Simple anharmonic oscillator models indeed account for the location of such transitions. It seems to us that in the common view most of the vibrational oscillator

strength is concentrated in these local modes, and that complicated nonseparable modes can be expected to be spectroscopically very nearly invisible. Does this view have a basis in the physics of the problem?

We wish to point out that a simple semiclassical argument readily rationalizes the observations and the common view. In the following the transition probability is computed as an average over all initial stationary states that lie within a