

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

narrow energy range E_i to $E_i + \delta E$. The resulting quantal spectrum can then be readily evaluated as a phase space integral.⁷

The normalized, averaged quantal spectrum at the frequency ω (with $\hbar = 1$) is given by

$$S(\omega) = \sum_i \sum_f |\langle f | \hat{d} | i \rangle|^2 \delta(E - E_i) \delta(E + \omega - E_f). \quad (1)$$

Here, \hat{d} is the transition dipole operator whose classical analog is the dipole function d . Replacing the last delta function in Eq. (1) by its Fourier representation, we obtain

$$S(\omega) = (2\pi)^{-1} \int dt \exp(i\omega t) \langle C(t) \rangle, \quad (2)$$

where $\langle C(t) \rangle$ is the dipole time autocorrelation function

$$\langle C(t) \rangle = \text{Tr} \{ \delta(E - H) \hat{d}^\dagger(t) \hat{d}(0) \} \quad (3)$$

and $\hat{d}(t)$ is the dipole operator in the Heisenberg picture. This differs from the usual form in the presence of the delta function in Eq. (3) which enables the trace to be replaced by its classical equivalent phase space integral

$$\langle C(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{2T} \left\langle \int_{-T}^T d(t + \tau) d(\tau) d\tau \right\rangle. \quad (4)$$

The angular brackets, in Eq. (4) and following, denote a phase space average.

We represent the classical dipole function as a sum over contributions from a complete set of linearly independent components $d = \sum_a d_a$. Each component d_a can represent a bond or a chromophore, for example, and is a function of one (or a few) coordinates. The classical analog $d(t)$ of the Heisenberg operator $\hat{d}(t)$ is obtained by time propagating the coordinates. Hence, as time increases the $d_a(t)$'s become functions of an increasing subset of all molecular coordinates. Therefore, each $d_a(t)$ can be expanded in the basis of the fixed d_b 's with time-dependent coefficients:

$$d_a(t) = \sum_b D_{ba}(t) d_b. \quad (5)$$

Equation (5) is to be understood as a classical version of a Heisenberg picture. We time propagate the observables while keeping the state (that is, the initial distribution in phase space) unchanged. The phase space average, assuming independent chromophores (i.e., $\langle d_a d_b \rangle = \delta_{a,b} \langle d_a^2 \rangle$), yields

$$\langle d(t) \rangle = \sum_a D_{aa}(t) \langle d_a^2 \rangle. \quad (6)$$

Here, $D_{aa}(t)$ is the time correlation function (i.e., the "survival probability"⁸) of the chromophore a . The averaged spectrum is then a superposition of contributions from the chromophores

$$S(\omega) = \sum_a \langle d_a^2 \rangle S_a(\omega), \quad (7)$$

where $S_a(\omega)$ is the Fourier transform of $D_{aa}(t)$. Equation (7) is our key result.

One can now consider two limiting situations. When the classical dynamics are highly chaotic, a typical trajectory covers most of the available phase space. The autocorrelation functions $D_{aa}(t)$ then rapidly decay from their initial value of unity and hardly, if at all, recur. Their long time values are low. Their Fourier transforms must in general be quite broad (reflecting the initial rapid decay) and devoid of details (reflecting the absence of recurrences). If, however, the motion does exhibit local mode characteristics then, by definition, one or more of the $D_{aa}(t)$'s must exhibit a recurrence. It is this recurrence which is reflected as a distinct spectral feature. A particular example of such features are the broad states recently⁹ noted in the stimulated emission spectrum of acetylene which have been interpreted as being due to local CH stretches.¹⁰

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