The density of reactive levels in NO_2 unimolecular decomposition

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Laser induced fluorescence spectra of expansion-cooled NO_2/Ne samples (1 and 2 K) are reported for transitions that originate from the lowest rovibronic levels and terminate on levels near D_0. At 1 K, nearly all transitions originate from $N''=0$. With the present resolution of 0.02 cm^{-1}, the 1 K spectra are resolved rather well. The high density of transitions is due to couplings between rovibronic levels with different N and K quantum numbers and with electronic characters that borrow oscillator strength from bright B_2 vibronic species of the mixed $^2A_1/^2B_2$ electronic system. Just above reaction threshold, such rovibronic species comprise the manifold of levels sampled by optically prepared wave packets. However, at higher energies we argue that the density of B_2 vibronic species is a more relevant parameter to describe the nature of unimolecular reactions. Nuances of the optical excitation process are discussed.

I. INTRODUCTION

The molecular density of states, $\rho(E)$, has been shown to be a useful entity in theories of chemical reactions in which statistical mechanics is used to treat collectively the properties of many individual levels. For example, microcanonical transition state theories make extensive use of the rate expression

$$k(E) = \frac{N^\ddagger(E-E_0)}{h\rho(E)}, \qquad (1)$$

where $N^\ddagger(E-E_0)$ is the number of open channels at the transition state and $\rho(E)$ is the density of reactant levels coupled to products. Accordingly, detailed experimental and theoretical studies of unimolecular decay processes have been pursued vigorously by a number of groups.[1-30] Most of this attention has been focused on the numerator of Eq. (1). However, for the determination of $N^\ddagger(E-E_0)$ from $k(E)$ measurements to constitute a useful exercise, $\rho(E)$ should be known independently, e.g., from measurements and/or empirical estimations.

In the majority of polyatomic molecules, $\rho(E)$ varies smoothly at chemically significant energies, where there are many states per wave number. However, in small systems, $\rho(E)$ should not be taken *a priori* to be a smooth function of energy with a well-defined, predictable dependence. In fact, differences have been reported between the $\rho(E)$ values obtained by extrapolating from lower energies vs the $\rho(E)$ values measured directly at chemically significant energies, and these differences have been shown to be important in several systems that are prototypical of small molecule unimolecular decomposition reactions.[31,32] With reference to Eq. (1), it is clear that $k(E)$ is influenced as much by $\rho(E)$ as it is by $N^\ddagger(E-E_0)$. Detailed studies of level densities near D_0 can be used to address these issues.

It is our thesis that small molecular systems provide the best means for establishing how complicated quantum mechanical behavior leads to experimental observations of statistical behavior. For example, transition state frequencies[33-37] as well as mappings of transition state levels onto product excitations[38,39] relate directly to $N^\ddagger(E-E_0)$

and reflect the quantized nature of the transition state in degrees of freedom orthogonal to the reaction coordinate.[14] Such experiments are usually carried out with optical preparation of the reacting levels. This yields good time or frequency resolution, but demands meticulous interpretation of the data.

Below D_0, NO_2 has 3 zeroth-order excited doublets of A_2, B_1, and B_2 electronic symmetries in addition to its $^2A_1$ ground state, as shown in Fig. 1. Low lying quartets are all repulsive except 1 $^4A'$, which is very weakly bound.[40] Optical excitation is known to prepare individual states of strongly mixed $^2A_1/^2B_2$ electronic character, i.e., a realization of the Douglas effect.[41] In the region 16 500–18 500 cm^{-1}, it was shown that the spectroscopically observed levels are restricted almost exclusively to B_2 *vibronic* species, which accounts for half the levels of the mixed $^2A_1/^2B_2$ *electronic* system.[42,43] At these energies, NO_2 is said to display vibronic chaos, since the distribution of B_2 vibronic nearest-neighbor level spacings fits a Wigner distribution.[43] At levels nearer to D_0, rovibronic interactions lend bright character to otherwise dark A_1 vibronic species, and the system displays more the character of rovibronic chaos.[44]

Many NO_2 spectra have been recorded below D_0 and considerable progress has been made recently in understanding the spectroscopy of this important species.[42-47] In the present study it is not our goal to *assign* spectra; we leave that to the experts.[42-47] We choose only to examine the density of optical transitions to see how this changes with energy, and to make a statement about the relationship between the density of levels that are accessed spectroscopically and the $\rho(E)$ that is used in Eq. (1).

When many levels are excited simultaneously, $\rho(E)$ represents a level-averaged quantity that can be used in Eq. (1), albeit with weightings as per electric dipole excitation. On the other hand, when a small number of levels is excited, $\rho(E)$ may be ill-defined, appearing to vary considerably with small energy increments. Thus, deducing and applying $\rho(E)$ requires care, particularly when optical excitation is used to prepare reactive species. Symmetries and optical selection rules, couplings between electronic states (i.e., other than the strongly mixed $^2B_2/^2A_1$ electronic system), anharmonicities,
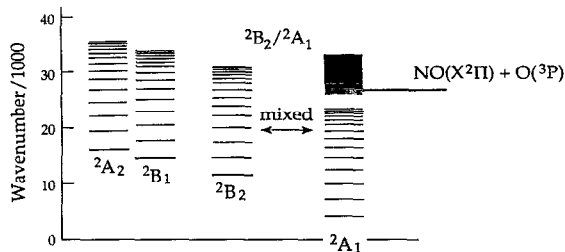
FIG. 1. Diagram showing energetically accessible doublets. Quartets are repulsive except for a slightly attractive part of the 1 $^4A'$ surface.

FIG. 2. Schematic drawing of the experimental arrangement.

rovibronic interactions, excitation bandwidth, and coherence, etc. must all be dealt with in obtaining $\rho(E)$ at chemically significant energies. Strictly speaking, the density of molecular levels diverges above D_0, requiring careful consideration of couplings between zeroth order bound levels and the continuum. Due to the richness of the NO_2 energy level structure, these problems are more severe than with other small molecules.

In this paper, we report the density of NO_2 optical transitions that originate from ground state molecules (i.e., $N_{K_aK_c}=0_{00}$) and terminate on levels near the dissociation threshold. The experiments are similar to those reported recently by Miyawaki et al.,[3(a)] but with a factor of 2–3 better resolution. At our present experimental resolution of approximately 0.02 cm^{-1}, spectral features appear to be mostly resolved except for hyperfine structure. The density of observed transitions varies and fluctuates dramatically, and depends on weightings as per absorption cross sections and one's choice of energy resolution. Nonetheless, there is a persistent maximum just below D_0 that can be ascribed to the *sharing* of oscillator strength amongst levels, i.e., the low resolution absorption coefficient is approximately constant in this spectral region.

The reported level densities just below D_0 are compared with extrapolations from lower energies, e.g., the 16 500–18 500 cm^{-1} region where the density of B_2 vibronic levels was found to be approximately 0.1/cm^{-1}.[43] Additionally, the experimental densities are discussed in terms of implications for photoinitiated unimolecular decomposition studies.[33–35] Specifically, we elaborate on how the density of spectroscopic transitions below D_0 is related to $\rho(E)$ in Eq. (1) at small and large excitations over the reaction threshold. We argue that in the region just above D_0, where the unimolecular decay rate is comparable to Coriolis and spin-rotation couplings, full rovibronic analyses should be invoked to describe the manifold of reactive states accessed optically. On the other hand, several hundred wave numbers above D_0, where the unimolecular decay widths are relatively broad, the optically accessed reactive manifold is best described as B_2 vibronic levels of the mixed $^2A_1/^2B_2$ electronic system.

We note that the electronic spectroscopy of NO_2 has been studied more than that of any other small molecule, making it impractical to provide a comprehensive list of references. However, the recent work of Jost and co-workers is unequivocally the most detailed spectroscopic study of this
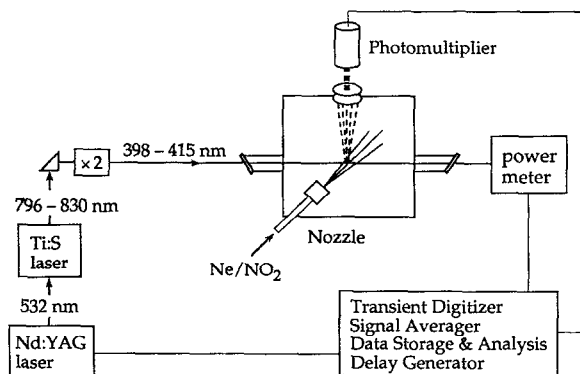
molecule to date in the high energy regime.[42,43,47] Above D_0, recent spectroscopic studies have been involved with understanding the couplings to the continuum and the detailed unimolecular decomposition mechanism, including interferences and fluctuations,[39] product state distributions,[2(e),2(f),3(a)–3(c),8] and time and frequency domain rate measurements.[3(a),33,34] We will draw most heavily from experimental and theoretical results that have been reported since 1990.

II. EXPERIMENTAL ARRANGEMENT AND RESULTS

The experimental arrangement is shown schematically in Fig. 2. Laser induced fluorescence (LIF) spectra of expansion cooled samples were recorded by using the doubled output (10 mJ cm^{-2}) of a titanium-doped sapphire (Ti:S) laser (Continuum/STI, HRL100Z); linewidths near 25 000 cm^{-1} were approximately 0.02 cm^{-1}. All spectra were normalized for fluctuations in the laser energies. In order to minimize Doppler broadening, only the central-most portion of the expansion was imaged onto the cathode of the photomultiplier tube. Such LIF experiments are quite straightforward and more detailed descriptions can be found in the literature.[1–4]

The expansion conditions were varied in order to obtain either *cold* rotational temperatures of ~1 K or *warm* rotational temperatures of ~2 K. Typically, 0.2% NO_2 in Ne at a backing pressure of ~5 atm yielded ~1 K, while 2.4% NO_2 in Ne at ~1.7 atm yielded ~2 K. By comparing spectra recorded at these two temperatures, it is easy to identify transitions that arise from rotationally excited (i.e., $N=2$) levels. NO_2 rotational temperatures were determined quantitatively by using the assigned features near 23 625 cm^{-1},[42] as shown in Fig. 3.

The LIF spectrum recorded in the interval 0–3.35 cm^{-1} below D_0 is shown in Fig. 4. This spectrum results from the raw data being subjected to a 3-point smoothing routine, which lessens high frequency noise without altering the information. As stated in the Introduction, our goal is to determine the density of transitions rather than make spectroscopic assignments. Consequently, no attempt has been made to establish absolute frequencies. Nearly all of the lines originate from the lowest rotational level; those that do not
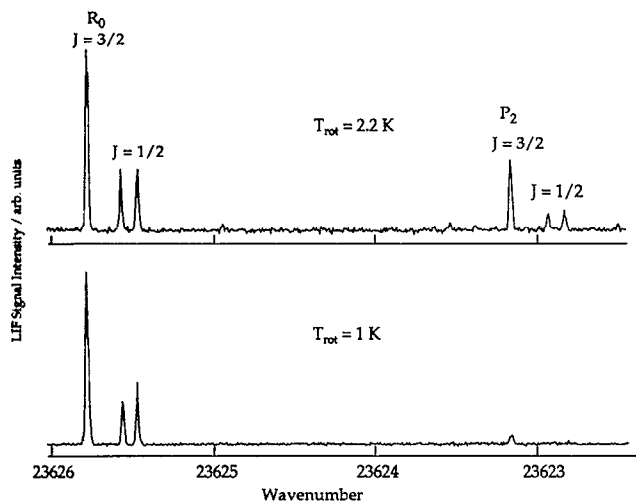
FIG. 3. Typical spectra from which NO$_2$ rotational temperatures were determined. Assignments have been made by Delon et al. (Ref. 42). P_2 transitions originate from $N=2$; notice the large difference for T_{rot} values of 1 and 2.2 K.
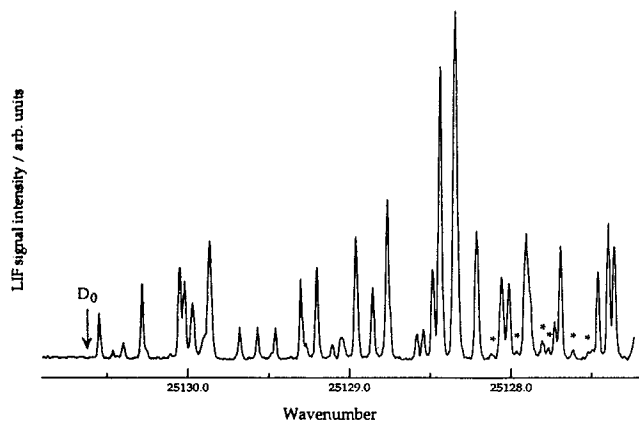

FIG. 4. LIF spectrum for the region 0–3.5 cm^{-1} below D_0 (whose approximate location is indicated by a vertical arrow). Asterisks mark transitions originating from excited rotational levels. The wave number scale is approximate.
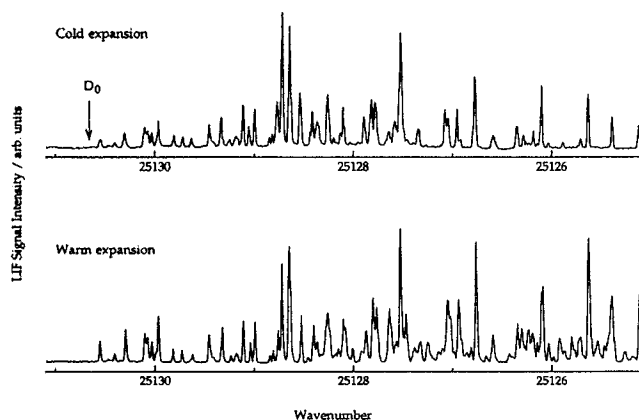

FIG. 5. The cold (1 K) spectrum has few contributions from excited rotational levels while the warm (2 K) spectrum has many. By comparing relative peak heights, it is possible to isolate transitions that originate from $N''=0$. The wave number scale is approximate.
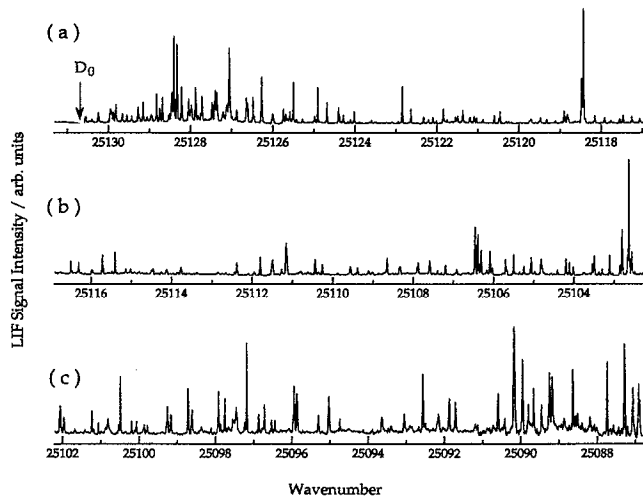

FIG. 6. Taken end-to-end, panels (a)–(c) cover D_0-E values from 0 to 45 cm^{-1}. The wave number scale is approximate.

are marked by asterisks. This spectrum is similar to the one reported by Miyawaki et al.[3(a)] However, the present spectrum was recorded with a factor of 2–3 higher resolution, enabling nearly all of the features other than the hyperfine structure to be resolved. Accordingly, the density of observed transitions in the region 0–5 cm^{-1} below D_0 increased from 8.2/cm^{-1} to 10/cm^{-1}. Note that within 2.54 cm^{-1} of D_0, transitions that originate from $N''=2$ rotational levels cannot contribute to the spectrum, since one photon excitation transports these rotationally excited molecules to energies above D_0, where dissociation is rapid relative to spontaneous emission.

Figure 5 shows a portion of the spectrum recorded with both warm (2 K) and cold (1 K) expansions. Spectra of the cold expansion covering the 45 cm^{-1} region below D_0 are shown in Fig. 6. As stated above, careful comparisons of warm and cold spectra enable us to assign transitions that originate from the 0_{00} level. Cold expansion spectra recorded 480 cm^{-1} below D_0 are displayed in Fig. 7. Note the different densities of transitions in Figs. 6 and 7.

Figure 8 shows the number of observed transitions $N(E)$ plotted vs energy for the range 0–40 cm^{-1} below D_0. The
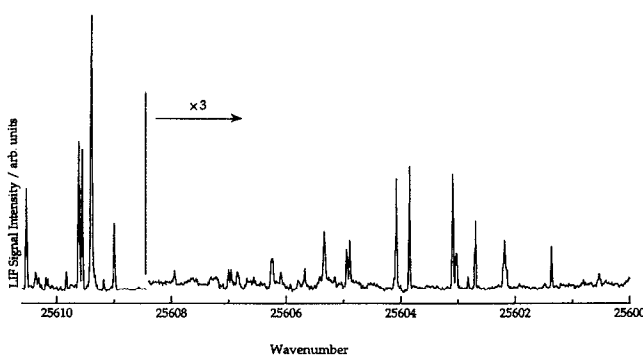

FIG. 7. Spectrum recorded ~480 cm^{-1} below D_0. Note the ×3 scale expansion. The wave number scale is approximate.

FIG. 8. Number of observed transitions vs energy, relative to D_0-45 cm^{-1}. The transitions are from the spectrum shown in Fig. 6.

levels are counted relative to D_0-40 cm^{-1}. Figure 9 shows the corresponding densities of states $dN(E)/dE$ for 3 different resolution windows, 0.5, 2, and 8 cm^{-1}, for (a), (b), and (c), respectively. One sees that the average density of ~ 5/cm^{-1} only obtains from averaging over fluctuations, which can be considerable with high enough resolution.

III. DISCUSSION

A. Relating the density of observed transitions to the density of energy levels

At least in principle, it is possible to relate the measured density of optical transitions that terminate on levels below D_0 to the corresponding densities of vibronic and rovibronic levels, albeit without specific vibronic assignments of the excited states. In turn, this can provide a basis for discussing the nature of the levels above D_0 that comprise the manifold sampled by wave packets during the course of unimolecular decay. All of the NO$_2$ levels above D_0 are known to dissociate, and with few exceptions the optical resonances that access these dissociative levels are overlapped, but not severely.[23,29] Under these conditions, with sufficient experimental energy resolution, fluctuations in rates can be
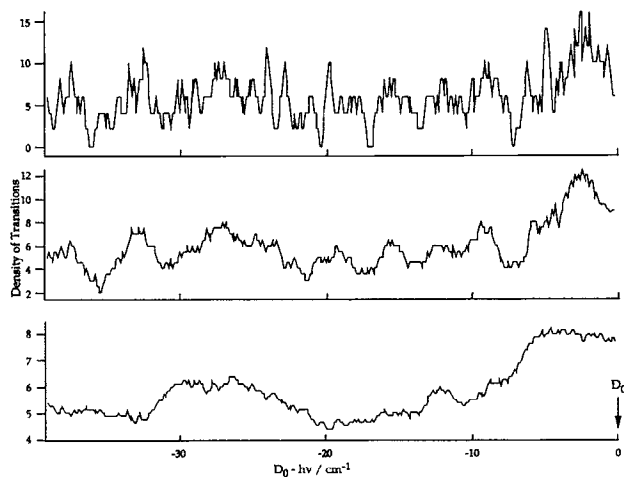

FIG. 9. Densities of transitions for the spectrum shown in Fig. 6. Panels (a), (b), and (c) are for energy resolution windows of 0.5, 2, and 8 cm^{-1}, respectively.

observed,[31] and a steplike variation of $k(E)$, reflecting the opening of reactive channels, can also be observed,[3(a)] for example, when averaging over fluctuations.

Defining the level density used in Eq. (1) requires care. Above dissociation threshold, bright B_2 vibronic levels are coupled to a variety of dark molecular levels as well as to the NO+O continuum. The couplings to the continuum both fluctuate[3(a)] and increase (on average) with energy. Specifically, what will be the evolution of optically prepared wave packets? On the way to products, will they visit states that are best described as rovibronic, vibronic, B_2 vibronic, etc.? Does the manifold of states sampled vary with $E^\dagger$, and if so, what guidelines should be used? For example, a few wave numbers above D_0, couplings to the continuum may be so weak that the packet first spreads over a variety of rovibronic levels which are similar in character to those observed just below D_0. However, it is unlikely that this remains true at higher $E^\dagger$, say hundreds of wave numbers. Here, couplings to the continuum are relatively strong (i.e., decay widths are at least several wave numbers[34]) and it is believed that reaction proceeds via a somewhat tight transition state for a reaction having no reverse barrier, as has been seen in variational RRKM calculations on this system.[19(a)] In this regime, the reacting molecules experience vigorous intramolecular vibrational dynamics and they may be oblivious to more subtle dynamical details, such as those whose classical motions have relatively long recurrence times.[21] In the discussion that follows, these issues will be addressed.

B. Transitions terminating on levels below D_0: Theoretical considerations

Our first goal is to relate the density of observed spectral lines that terminate on levels below D_0 to the corresponding density of states. To begin, NO$_2$ levels are classified according to symmetry species and an overview of the relevant optical selection rules is provided.

At the lowest level of approximation, the Born–Oppenheimer wave function of a particular state is written as a product of electronic, vibrational, and rotational parts,

$$\psi_{EVR} = \psi_E \psi_V \psi_R. \tag{2}$$

The ground electronic and vibrational wave functions of NO$_2$ are fully symmetric A_1 species of the C_{2v} symmetry group, and the lowest rotational levels populated in a typical supersonic expansion, i.e., even N'' and $K''=0$, are also A_1. Were the Born–Oppenheimer approximation to hold, the vibrational and rotational selection rules for the $^2B_2 \leftarrow ^2A_1$ electronic transition would be $A_1 \leftarrow A_1$ and $B \leftarrow A_1$, respectively. The symmetry of optically prepared vibronic species (i.e., $\psi_E \psi_V$) is $B_2 \otimes A_1 = B_2$, and the symmetry of the full wave function is $B_2 \otimes B_1 = A_2$. To simplify notation, we will refrain from using single primes to label the optically prepared levels.

It is well known that NO$_2$ has a conical intersection between the ground $^2A_1$ and excited $^2B_2$ electronic surfaces.[29,30] As a result, species having the same *vibronic* symmetry but different *electronic* symmetries are mixed strongly, forming manifolds of A_1 and B_2 vibronic species, with only the B_2
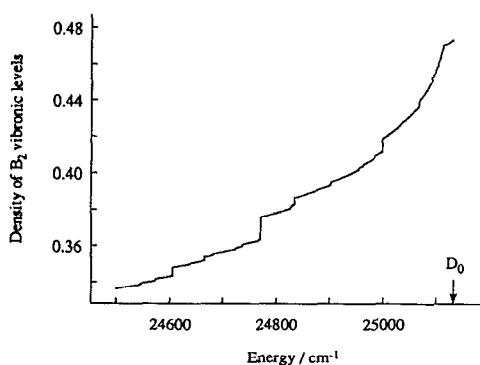
FIG. 10. Calculated density of B_2 vibronic levels on the $^2A_1$ electronic surface vs energy for the region near D_0. The method and molecular constants of Toselli and Barker were used (Ref. 48).

vibronic species optically accessible from the ground state. The excited-state wave function is written as a product of the rotational and vibronic parts,

$$\psi_{EVR}(A_2) = \psi_R(B_1)\left[\psi_E(^2B_2)\sum C_\beta\psi_{V,\beta}(A_1) \right.$$

$$\left. + \psi_E(^2A_1)\sum C_\alpha\psi_{V,\alpha}(B_2) \right]$$

$$= \psi_R(B_1)\psi_{EV}(B_2), \qquad (3)$$

where the summations are taken over the vibrational levels of the $^2B_2$ and $^2A_1$ electronic manifolds. As discussed below, other electronic states may participate near reaction threshold. Without considering spin, nor with additional interactions that compromise the separability of rotational and vibronic degrees of freedom, the density of optical transitions is given by $2\rho_{EV}(B_2)$ for $N''>0$ and by $\rho_{EV}(B_2)$ for $N''=0$, where $\rho_{EV}(B_2)$ is the total density of B_2 vibronic levels for the mixed $^2A_1/^2B_2$ system, and the factor of 2 reflects the $N'' + 1 \leftarrow N''$, $\Delta K = 0$ rotational selection rules.

Figure 10 presents the density of B_2 vibronic levels for the $^2A_1$ electronic surface calculated by using the coupled-oscillators model developed by Toselli and Barker.[48] This approach is preferred over others since it handles anharmonicities over a broad range of energies up to and above D_0. Unfortunately, the spectroscopic constants of Delon *et al.*[42,43] cannot be used with this scheme, since their multiterm expansion diverges at energies near D_0. Thus, the constants given by Toselli and Barker were used. This yielded excellent agreement with the Delon *et al.* densities in the region 16 500–18 500 cm^{-1}.

A glance at the experimental spectra indicates that the calculated level density shown in Fig. 10 differs significantly from the observed density of transitions. Though contributions from the $^2B_2$ electronic surface are not included in Fig. 10, this only increases the level density near D_0 by $\sim$20%.[49]

The above comparison suggests that additional interactions increase the number of optical transitions. The most likely candidates are Coriolis and spin-rotation couplings.

The former mixes rovibronic levels that have the same total symmetry, A_2, rotational quantum number, N, and angular momentum quantum number, J,

$$\psi_{EVR}(J,N,A_2) = \sum [C'\psi_R(J,N,B_1)\psi_{EV}(B_2)$$

$$+ C''\psi_R(J,N,A_2)\psi_{EV}(A_1)]. \qquad (4)$$

This couples B_2 and A_1 vibronic species, which doubles the number of accessible vibronic levels, and destroys K quantum numbers by mixing together all values of K having the proper symmetry, i.e., every other one. The latter increases the density of optically accessible states by a factor of $(N + 1)/2$ or $N/2$ for odd or even N, respectively. Finally, spin-rotation interaction couples wave functions $\psi_{EVR}(J,N,A_2)$ of a given J, but having different values of N,

$$\psi(J,A_2) = C^{(+)}\psi_{EVR}(J,J + 1/2,A_2) + C^{(-)}$$

$$\times \psi_{EVR}(J,J - 1/2,A_2). \qquad (5)$$

As a result, N is not a good quantum number above $\sim$20 000 cm^{-1},[42,43] and for a given J value, N takes on both odd and even numbers. For the complete breakdown of K and N, the number of accessible levels is multiplied by $(2J + 1)/2$. The latter, combined with the breakdown of A_1 and B_2 vibronic symmetries, brings the density of optical transitions originating from the $N''=0$ rotational level up to $(2J + 1)\rho_{EV}(B_2)$ for a given value of J. Note that this number is not enhanced by any other interactions unless electronic surfaces other than $^2B_2$ and $^2A_1$ come into play. This is because A_1 and A_2 are exact symmetry species of NO$_2$ originating from exchange of identical nuclei, and therefore their mixing is strictly forbidden.

As discussed in the experimental section, cold spectra consist of transitions originating from the ground rotational state, $J''=1/2$. Therefore, the angular momentum quantum number of the optically prepared A_2 species has only two values (i.e., $J_1 = 1/2$ and $J_2 = 3/2$) and the density of spectral lines for the case of complete K and N breakdown is the combined density for these two J values,

$$(2J_1 + 1)\rho_{EV}(B_2) + (2J_2 + 1)\rho_{EV}(B_2) = 6\rho_{EV}(B_2). \qquad (6)$$

Using the density of vibronic species for just the $^2A_1$ ground electronic surface presented in Fig. 10, one derives densities of 2.1, 2.6, and 2.9 transitions/cm^{-1} at $D_0 - E = 500$, 50, and 5 cm^{-1}, respectively. The densities for the mixed $^2A_1/^2B_2$ system are expected to be approximately 20% higher,[49] i.e., 2.5, 3.1, and 3.4 transitions/cm^{-1}, respectively.

C. Transitions terminating on levels below D_0: Experimental considerations

Estimating the density of lines from experimental spectra is subjective. Couplings between bright and dark levels fluctuate dramatically and may also be rather modest for a number of the levels. Counting levels under such conditions is largely a matter of experimental signal to noise ratio and one's ability to distinguish intrinsically weak lines from hot bands.

As shown in Figs. 8 and 9, the density of observed transitions is not a smooth function of energy. In fact it obtains

its largest value—by about a factor of 2 in this energy range—just below D_0. Leaving aside for the moment the high-density behavior observed within several wave numbers of D_0, the density of transitions is still quite high (i.e., ~5/cm^{-1} on average) over the 45 cm^{-1} below D_0. At ~500 cm^{-1} below D_0, the density of transitions is somewhat lower (i.e., ~3.5/cm^{-1} on average); however, it is still noticeably higher than the calculated value. The discrepancy can be rationalized by ascribing the difference to excited electronic states (e.g., $^2B_1$ and $^2A_2$) that are coupled to the mixed $^2A_1/^2B_2$ system. Alternatively, the coupled-oscillators model may underestimate anharmonicities, leading to low densities near D_0.

In a recent spectroscopic study, Delon *et al.* assigned $J'=1/2$ and $3/2$ levels by recording R_0 and P_2 transitions at 150 MHz resolution.[50] The number of transitions terminating on $J'=3/2$ was compared to the number terminating on $J'=1/2$. The ratio of these numbers, $[3/2]/[1/2]$, was found to be 1.13 between 16 600 and 18 500 cm^{-1} and 1.41 between 23 350 and 23 950 cm^{-1}. For the case of complete K and N breakdown, the $[3/2]/[1/2]$ ratio is 2. It will be interesting to see how this ratio varies as the dissociation threshold is approached; this work is in progress.[51]

The region very close to D_0 appears unique in that the density of transitions doubles within 5 cm^{-1} of D_0. Is this an accidental clump of states, or are there interactions in a barely bound molecule that cause additional mixing with other electronic states? For example, as pointed out by the reviewer, many electronic states are nearly degenerate for large bond extensions, thus facilitating their mixing and possibly accounting for the high state density within 5 cm^{-1} of D_0. Specifically, repulsive curves that would be inaccessible at shorter bond extensions can participate. Since the present experimental results do not provide a definitive answer, these issues are left for further enquiry.

Our main conclusion regarding level densities below D_0 is that the extrapolated values of the densities of B_2 vibronic levels are within a factor of 2 of those obtained by using the density of observed transitions (~5/cm^{-1} throughout the range $5 \leqslant D_0 - E \leqslant 45$ cm^{-1}), together with the assumption of complete rovibronic mixing of A_1 and B_2 vibronic species in the $^2A_1/^2B_1$ electronic system. For example, near D_0 (but not within 5 cm^{-1}), the B_2 vibronic densities obtained from the extrapolation and from the observed transitions are 0.47/cm^{-1} and 0.83/cm^{-1}, respectively. The reason for the difference is not obvious, but might include significant anharmonicity and/or other electronic states that are coupled to the bright states by weak spin–orbit, spin-rotation, and Coriolis interactions.

D. Implications for $k(E)$

As stated earlier, defining the level density used in Eq. (1) requires care. For example, strictly speaking, the density of states is infinite above the reaction threshold. Of course, the $\rho(E)$ used in Eq. (1) is for the reactant part of the overall system. Therefore, we take $\rho(E)$ to be that of the NO₂ molecule with a boundary at the transition state that separates

reactants from products. Furthermore, it is known that the location of the transition state depends on the available energy.[18,19]

Just above reaction threshold, Miyawaki *et al.* reported that the rate rises in steps whose energy increments are those of the NO rotational quanta, i.e., according to PST.[52] This PST-like behavior suggests that the transition state is located at large interfragment separations. However, at higher energies the transition state moves inward and the $k(E)$ steps associated with the opening of new channels occur with larger energy increments, i.e., corresponding to NO₂ bending or hindered rotor vibrations. This tightening of the transition state is predicted by variational transition state theories.[14,18,19] For NO₂, it has been observed in our time-resolved measurements of NO₂ dissociation dynamics,[34] as well as in the variational RRKM calculations of Klippenstein and Radivoyevitch[19(a)] and in the quantum chemistry calculations of Katigiri and Kato.[40]

Toselli and Barker modeled the density of NO₂ vibronic levels above as well as below D_0.[48] At energies above D_0, they assumed a loose transition state located at the outer turning point of the highest bound level. This assumption is reasonable for energies close to D_0. At higher energies, this approach is likely to overestimate $\rho_{EV}(E)$ somewhat, since it does not take into account the inward shift of the transition state with increasing energy. Overall, the calculations of Toselli and Barker demonstrate nicely how the opening a reactive window affects the density of molecular states. The rise of $\rho_{EV}(E)$ is shown to be modest, and therefore we take as a first approximation that the density of *vibronic* states does not change when the energy passes the reaction threshold.

Should one use vibronic or rovibronic levels for the level density and the number of open channels in Eq. (1)? We argue that the answer depends on the excess energy. Just above reaction threshold, couplings to the continuum are weak, and broadenings of individual rovibronic levels do not smear their positions significantly or result in undue overlap. Under these conditions, the rate increases with energy as per PST, i.e., in increments of NO rotational quanta. In other words, the decay rate exhibits features on the energy scale of rovibronic interactions, and these features are governed by the rovibronic level structure of the loose transition state. Therefore, the number of rovibronic open channels should be determined for the specified full symmetry and angular momentum, and the same level of sophistication must be used for the density of states. The rate is then given by

$$k(E,J,A_2) = \frac{N^{\ddagger}(E,J,A_2)}{h\rho(E,J,A_2)}. \tag{7}$$

This is consistent with experimental estimations of rates based on lifetime broadenings,[3(a)] in which the rates were found to increase with small energy increments in the threshold region.

As the excess energy increases, the transition state moves inward and steps in the reaction rate are observed that correspond to bending or hindered rotation at the transition state. Under these conditions, steps that correspond to individual NO rovibronic open channels are not resolved in

$k(E)$. In terms of the above formulas, the level density $\rho(E,J,A_2)$ is given by $(2J+1)\rho(E,B_2)$ and the number of open channels $N^{\ddagger}(E,J,A_2)$ is given by $(2J+1)N^{\ddagger}(E,B_2)$. Thus, the $(2J+1)$ terms associated with the breakdown of K and N as good quantum numbers cancel in the expression for $k(E)$, yielding the RRKM formula for nonrotating molecules. In this region, the rate should increase in steps of roughly 7×10^{10} s^{-1} for the $\rho(E,B_2)$ value of approximately 0.5/cm^{-1} given in Fig. 10. The experimental steps are larger by roughly a factor of 2, i.e., $\sim1.3\times10^{11}$ s^{-1} at $E^{\dagger}\sim200$ cm^{-1}.

The cancellation at higher energies of the $(2J+1)$ factors in the numerator and denominator of Eq. (7) hints that fine rovibronic interactions are no longer needed to describe the unimolecular reaction. This can also be stated in terms of time-dependent quantum mechanics. For example, the $t=0$ wave packet prepared by a short pulse is best described as a zeroth order bright state (i.e., B_2 vibronic with $N=1$, $K=0$) optically coupled to the ground state. This is a coherent superposition of rovibronic and continuum levels. Due to Coriolis and spin-rotation interactions, the packet spreads over dark states with a rate $\sim\omega_{bd}$, where ω_{bd} is the Rabi frequency for perturbations that mix bright and dark levels. At sufficiently high excitations above D_0, reaction rates are faster than ω_{bd}, and the packet evolves to the product channel before loosing its N, K, and vibronic identity. Under these conditions, the packet senses only a B_2 vibronic phase space in both the molecular and transition state regions.

This description is equivalent to the standard argument about hierarchies of time scales in which fast dynamics are reflected in coarse spectral features while finer spectral details evolve only at longer times.[21] In the simplest of terms, reacting molecules leave the bound region of the PES before they can sense subtleties. For example, at $E^{\dagger}=500$ cm^{-1} the dissociation rate is known to be almost 10^{12} s^{-1}. By comparison, typical Coriolis and spin-rotation coupling matrix elements are generally no larger than a few tenths of a wave number,[47] corresponding to Rabi frequencies $\omega_{bd}<10^{11}$ s^{-1}. Consequently, it is not advisable to use a density of states and $N^{\ddagger}$ that incorporate complete rovibronic mixing, since the dynamics do not permit this level of detail to be seen on the time scale of the unimolecular reaction. The density of states will then be that of B_2 vibronic levels, taking us back to extrapolations such as those of Toselli and Barker[48] and of the Delon *et al.* data.[43]

We conclude that the levels used for $\rho(E)$ in the denominator of Eq. (1) depend on the respective strengths of the couplings to the continuum vs the interactions between zeroth order dark and bright levels. Though no mistake is made at higher energies when using the $N^{\ddagger}(E,J,A_2)$ and $\rho(E,J,A_2)$ given in Eq. (7), it is more meaningful to use only bright levels (i.e., B_2 vibronic) if $k\gg\omega_{bd}$. With $k\ll\omega_{bd}$, however, subtle rovibronic interactions can yield isolated levels that are each coupled to the continuum, with the additional aspect that the rates are expected to fluctuate considerably from one resonance to the next.[11(a),31] The same level of sophistication should be used for the transition state.

It appears that NO$_2$ corresponds to $k\sim\omega_{bd}$ just above D_0, lending support for the qualitative use of yield spectra,
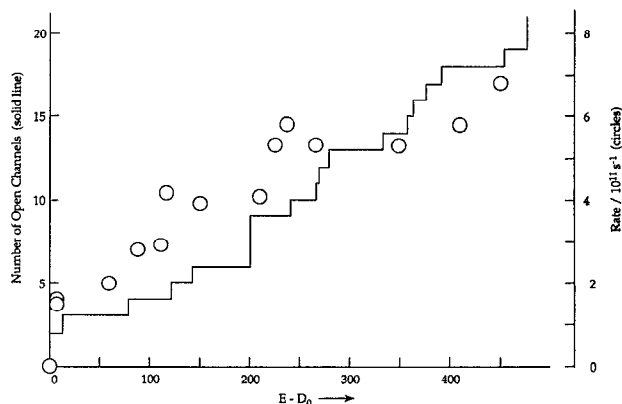

FIG. 11. Number of open channels vs $E-D_0$, from the theoretical study of Katigiri and Kato (Ref. 40). The open circles are the rate data from Ref. 34. Note the different vertical axes.

as demonstrated by Miyawaki *et al.*[3(a)] However, hundreds of wave numbers above D_0, the B_2 vibronic level density is the relevant parameter for use as $\rho(E)$ in Eq. (1). In this case, the extrapolated value of $\rho(D_0,B_2)$ yields steps in $k(E)$ vs E that occur in increments of $\sim7\times10^{10}$.

The above arguments implicitly assume that all levels are accessed with equal probability, which is not the case for optical excitation. As discussed below, bias in which level occupancies are weighted as per the dipole excitation process result in an effective density of states that is lower than the actual one.

E. Recent *ab initio* calculations

Recently, *ab initio* calculations at the state-averaged CASSCF level were carried out for the NO$_2\rightarrow$NO+O reaction by Katigiri and Kato,[40] who constructed adiabatic potential surfaces including spin–orbit interaction by using the full Breit–Pauli Hamiltonian. The evolution of the NO$_2$ bending degree of freedom along the reaction coordinate was examined to see its effect on the reaction dynamics. For the NO(X $^2\Pi_{1/2}$)+O($^3P_2$) limit, which is the most important channel at energies up to several hundred wave numbers above D_0,[3] it was shown that there is no discernible barrier for bending along the reaction coordinate for the first two open channels. However, higher levels show barriers which move inward to 2.9–3.0 Å, as reported by Klippenstein and Radivoyevitch.[19(a)] In Fig. 11, we have replotted the data shown in Katigiri and Kato's Fig. 9 in order to display the number of open channels vs $E-D_0$, thus drawing attention to the correspondence between these results and the previous rate measurements. Note that all of the A_1 and B_2 vibronic levels are present in the calculated $N^{\ddagger}$ values.

The calculations predict that $N^{\ddagger}$ rises abruptly at threshold, then more slowly, and then displays several steps. This behavior bears similarity to the results of the experimental $k(E)$ measurements, which are shown as open circles in Fig. 11.[33,34] Specifically, the experimental rates rise abruptly at threshold, then more slowly, and then two relatively flat steps appear. In fact, the crude steps formed by the bunching of adiabatic curves in the calculations surprised us. Is this for-

tuitous or is there more to it? Time will tell. In Fig. 11 the different quantities associated with the left and right vertical axes are related by ρ. Therefore a direct comparison cannot be made. However, for a constant ρ value of 0.75/cm^{-1}, the axes are equivalent, indicating the extent of the discrepancy. Detailed measurements of $k(E)$ using double resonance excitation will provide a more quantitative basis for comparison.

F. Optical excitation and effective level densities

Finally, we point out an obvious fact that is relevant to the discussion; that the simultaneous photoexcitation of many energy levels inevitably weights their participation as per the transition dipole matrix elements and phase coherences of the optical excitation step. This should be included in modeling the reaction dynamics. Even with incoherent phases, which is to be expected for the lasers used in our subpicosecond resolution experiments and the chaotic dynamics characteristic of unimolecular decomposition, the weightings of the optically accessed levels are such that those levels having larger matrix elements with the ground state are favored. This bias causes the effective number of participating levels to be smaller than the number of accessed levels per se in a given experiment. Several aspects of this phenomenon have been discussed previously.[34] As a consequence, the *effective* density of optically excited levels in experiments in which many levels are excited simultaneously is smaller than the actual level density, and this may account, at least in part, for the difference between the measured rates and those predicted on the basis of the $\rho(E,B_2)$ level density.

IV. SUMMARY

The following conclusions are germane to energies below D_0, i.e., where all of the spectroscopic data presented herein were obtained.

The number of observed transitions per wave number that originate from the ground rovibronic state (i.e., $N_{K_aK_c}=0_{00}$) is largest in the interval 0–5 cm^{-1} below D_0, where it is 10/cm^{-1}. In the interval 5–45 cm^{-1} below D_0 it is 5/cm^{-1} on average. At lower energies (i.e., 480 cm^{-1} below D_0) it is 3.5/cm^{-1} on average. The density of observed transitions rises rapidly with increasing energy, even though the low resolution absorption coefficient is approximately constant throughout this region, indicating that the available oscillator strength is shared.

A previous spectroscopic study by Delon *et al.* yielded a B_2 vibronic state density of 0.1/cm^{-1} in the range 16 500–18 500 cm^{-1}.[43] The calculation of Toselli and Barker[48] is in good agreement with the Delon *et al.* data and yields $\rho_{B2}(D_0)\sim 0.5$/cm^{-1}.

Recent work by Delon *et al.* indicates that the breakdown of K and N quantum numbers increases with energy.[50] Assuming complete rovibronic chaos, 5 transitions per wave number corresponds to 1.67 vibronic levels per wave number. In the event that this density is shared equally between A_1 and B_2 vibronic species, each will have a density of 0.84/cm^{-1}. The difference between this value and the extrapolated values is too large to be ignored. We conclude that

in the interval 5–45 cm^{-1} below D_0 the spectrum probably reflects unusually large anharmonicities and/or contributions from the $^2A_2$ and $^2B_1$ electronic states. At this time, we cannot be more specific.

The interval 0–5 cm^{-1} below D_0, where the density of transitions is approximately 10/cm^{-1}, may be unique in that long bond extensions are involved. This may facilitate the participation of electronic curves that are repulsive at shorter distances.

Estimating NO₂ level densities by using spectroscopic measurements is subjective, even below D_0. There exist more levels than are recorded spectroscopically, with the number of "observed" levels depending to a large degree on the experimental signal to noise ratio.

The following conclusions are germane to the region above D_0, i.e., where all of the photoinitiated unimolecular reactions occur.

Just above D_0, say the first 5 cm^{-1}, it is possible for many rovibronically chaotic levels to participate in the unimolecular decomposition reaction. At these energies coupling to the continuum is relatively weak, i.e., average decay widths are 0.15 cm^{-1}, the same order of magnitude as the rovibronic interactions. In this energy region, the transition state is loose, as described by phase space theory and by variational RRKM theory.

At $E^\dagger$ values of hundreds of wave numbers, unimolecular decay widths are typically several wave numbers, e.g., $\sim$5 cm^{-1} at $E^\dagger=500$ cm^{-1}.[34] At these energies, decay widths are larger than spin-rotation and Coriolis matrix elements between zeroth order bright and dark states. Consequently, the zeroth-order bright levels (i.e., levels of B_2 vibronic symmetry in the coupled $^2A_1/^2B_2$ electronic system) are the main participants in the reaction. Thus, more subtle rovibronic interactions need not be taken into account and vibronic analyses are sufficient for $N^\ddagger$ and ρ in Eq. (1).

When many levels are excited simultaneously via an electric dipole process, their participation reflects their respective oscillator strengths. This bias can cause the effective number of reacting levels to be less than the number of levels per se. This may help reconcile differences between measured rates and present estimates of $\rho(E,B_2)$.

Recently, Katigiri and Kato[40] carried out *ab initio* calculations at the state-averaged CASSCF level, including spin–orbit interaction. This study indicates that the transition state is loose for the first few open channels, but quickly tightens, moving inward to 2.9–3.0 Å, in agreement with earlier theoretical work.[19(a)] Steplike $k(E)$ behavior is indicated, in agreement with experiments.[33–35] Their results are consistent with an effective level density close to that expected for B_2 vibronic species, in accord with the arguments presented herein.

ACKNOWLEDGMENTS

their most recent work on K and N breakdown at high energies. Research was supported by the U.S. Army Research Office and the National Science Foundation.

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