# Mechanism of NO<sub>2</sub> Photodissociation in the Energy-Deficient Region at 404.7 nm

Jack G. Calvert,\* Sasha Madronich, Edward P. Gardner, James A. Davidson, Christopher A. Cantrell, and Richard E. Shetter

National Center for Atmospheric Research,<sup>†</sup> Boulder, Colorado 80307 (Received: September 8, 1987; In Final Form: October 16, 1987)

The photodissociation of NO<sub>2</sub> for  $\lambda > \lambda_{diss}$  (397.9 nm) was restudied in view of the observed temperature dependence of its absorption cross section in the 404.7-nm region. It is hypothesized that the cross section for vibrationally excited molecules of NO<sub>2</sub> is greater than that for vibrationless molecules. This leads to the conclusion that NO<sub>2</sub> molecules excited in the energy-deficient region at 404.7 nm, which photodissociate, derive the required energy not only from rotational excitation as suggested in earlier studies but also from vibrational excitation. Use of this hypothesis leads to a reasonable fit of experimental and theoretical estimates of the quantum yields of NO<sub>2</sub> photodissociation at 404.7 nm as a function of temperature.

### Introduction

The photodissociation of  $NO_2$ , reaction 1, extends to wavelengths longer than the photodissociation limit, 397.9 nm.

$$NO_2 + h\nu \to O(^{3}P) + NO$$
(1)

This observation was first rationalized by Pitts et al.,<sup>1</sup> who proposed that the unexpected dissociation of NO<sub>2</sub> results from the utilization of internal rotational energy of the NO<sub>2</sub> molecules as well as the electronic energy of the excited molecule. Although this explanation is in qualitative accord with theory and the observed temperature dependence of the quantum yield ( $\phi_1$ ) measured in the wavelength range of energy deficiency,<sup>1-4</sup> the values of  $\phi_1$  predicted from this simple theory are from 43% to 17% lower than those observed experimentally.<sup>4</sup> Observations of the temperature dependence of the absorption cross section in experiments at 404.7 nm reported here suggest that the participation of vibrationally excited NO<sub>2</sub> molecules in the photodissociation at this wavelength may be greater than previously thought. A model based upon this premise brings the experimental and theoretical values of  $\phi_1$  into reasonable accord.

#### **Experimental Methods**

Measurements were carried out using the same large photolysis cell and associated equipment that was employed by Gardner et al.<sup>4</sup> The cell (155.8-cm optical path) was jacketed so that the temperature could be controlled by circulation of a temperature-controlled supply of bath fluid (ethylene glycol-water mixture). The 404.7-nm band of the mercury-xenon arc (Osram, 1000 W) was separated by means of a grating monochromator (Jarrell-Ash, 82-400) with 0.5-mm entrance and exit slits. This provided a near triangular band of about 1.6-nm resolution at one-half peak height. These are the same experimental conditions used by Gardner et al.<sup>4</sup> to measure the  $\phi_1$  values at 404.7 nm. The background (lamp shutter closed) and  $I_0$  (shutter open) photomultiplier tube (RCA 8575) counts were integrated over a 5-min interval prior to filling the evacuated cell. Then a measured pressure of purified NO<sub>2</sub> (0.2-0.4 Torr) was introduced, the gas was circulated for about 15 min, the lamp shutter was opened, and the photomultiplier tube was allowed to stabilize for 1 or 2 min. The transmitted light intensity was then measured. Decomposition of the NO<sub>2</sub> was negligible during the measurements. The pressure of NO2 employed at each temperature was controlled so that the N2O4 in equilibrium with the NO2 amounted to less than 1% of the  $NO_x$ . No significant light absorption by  $N_2O_4$  occurs in the 404.7-nm region.<sup>5</sup> Redundant cross section measurements were made in separate experiments by diluting a known amount of  $NO_2$  in  $O_2$  (large excess) and introducing this mixture into the cell without closing the shutter to the light source. The cross sections determined by both techniques gave nearly equal values. The averages of the measurements in experiments at

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TABLE I: Comparison of Theoretical and Experimental Estimates of  $\phi_1$  as a Function of Temperature ( $\lambda_{exc}$  near 404.7 nm)

|               |   |   |   | $\boldsymbol{\varphi}_1$   |  |  |
|---------------|---|---|---|--|--|--|
| $X_{\rm rot}$ | $1 - X_0$   | $\phi_{ m vib}$   | $\phi_{\rm rot}$  | theory   | expt   | ref <sup>a</sup>                                       |
| 0.142         | 0.00815   | 0.036   | 0.137   | 0.17   | 0.26   | 8  |
| 0.217         | 0.0203  | 0.087   | 0.198   | 0.29   | 0.327  | 4  |
| 0.253         | 0.0288  | 0.120   | 0.223   | 0.34   | 0.365  | 4  |
| 0.291         | 0.0397  | 0.160   | 0.244   | 0.40   | 0.39   | 4  |
| 0.321         | 0.0498  | 0.194   | 0.259   | 0.45   | 0.42   | 4  |
| 0.350         | 0.0615  | 0.232   | 0.269   | 0.50   | 0.46   | 4  |
| 0.393         | 0.0818  | 0.291   | 0.279   | 0.57   | 0.51   | 1  |
| 0.485         | 0.141   | 0.430   | 0.276   | 0.71   | 0.71   | 1  |
| 0.543         | 0.192   | 0.522   | 0.260   | 0.78   | 0.91   | 1  |
|               | X <sub>rot</sub><br>0.142<br>0.217<br>0.253<br>0.291<br>0.321<br>0.350<br>0.393<br>0.485<br>0.543 | $\begin{array}{c ccc} X_{\rm rot} & 1-X_0 \\ \hline 0.142 & 0.00815 \\ 0.217 & 0.0203 \\ 0.253 & 0.0288 \\ 0.291 & 0.0397 \\ 0.321 & 0.0498 \\ 0.350 & 0.0615 \\ 0.393 & 0.0818 \\ 0.485 & 0.141 \\ 0.543 & 0.192 \\ \end{array}$ | $\begin{array}{c cccc} X_{\rm rot} & 1-X_0 & \phi_{\rm vib} \\ \hline 0.142 & 0.00815 & 0.036 \\ 0.217 & 0.0203 & 0.087 \\ 0.253 & 0.0288 & 0.120 \\ 0.291 & 0.0397 & 0.160 \\ 0.321 & 0.0498 & 0.194 \\ 0.350 & 0.0615 & 0.232 \\ 0.393 & 0.0818 & 0.291 \\ 0.485 & 0.141 & 0.430 \\ 0.543 & 0.192 & 0.522 \\ \end{array}$ | $\begin{array}{c ccccc} X_{\rm rot} & 1-X_0 & \phi_{\rm vib} & \phi_{\rm rot} \\ \hline 0.142 & 0.00815 & 0.036 & 0.137 \\ 0.217 & 0.0203 & 0.087 & 0.198 \\ 0.253 & 0.0288 & 0.120 & 0.223 \\ 0.291 & 0.0397 & 0.160 & 0.244 \\ 0.321 & 0.0498 & 0.194 & 0.259 \\ 0.350 & 0.0615 & 0.232 & 0.269 \\ 0.393 & 0.0818 & 0.291 & 0.276 \\ 0.485 & 0.141 & 0.430 & 0.276 \\ 0.543 & 0.192 & 0.522 & 0.260 \\ \hline \end{array}$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

<sup>*a*</sup>References from which experimental  $\phi_1$  data were taken.

temperatures 273.2, 298.1, 325.2, 347.2, and 370.2 K gave  $\sigma$  values (units of  $10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup>) of 5.82, 6.07, 6.16, 6.62, and 6.57, respectively. The precision between measurements at a given temperature was about 1%. Obviously, the  $\sigma$  values are strongly temperature dependent.

#### The Nature of the Photodecomposition of NO<sub>2</sub> at 404.7 nm

Various attempts to rationalize the values of the quantum yields of NO<sub>2</sub> photodissociation for excitation at 404.7 nm have failed.<sup>2-4</sup> The fraction  $(X_{rot})$  of the NO<sub>2</sub> molecules at a given temperature which contain rotational energy in excess of the energy deficiency for dissociation on excitation with a 404.7-nm light quantum can be calculated readily. For the  $NO_2$  molecule the rotational energy levels can be approximated from the simple relation for prolate symmetric top molecules, employing the appropriate spectroscopic constants for NO<sub>2</sub>:  $E(J,K)/cm^{-1} = (0.4220)(J)(J + 1) + (8.0012)$  $-0.4220)K^2$ . For K = 0, J is even only (0, 2, 4, ...), while the K > 0, all positive values of J are allowed.<sup>6,7</sup> The calculated relative population of rotational states as a function of rotational energy is shown in Figure 1 for the temperature of 298 K. Similar calculations were made for each of the temperatures for which  $\phi_1$  data exist. Figure 2 shows the fraction ( $X_{rot}$ ) of NO<sub>2</sub> molecules which have energies greater than some specified minimum energy  $(E_{\min})$ ; the curves a-i refer to temperatures of 223, 273, 298, 325, 347, 370, 398, 496, and 566 K, respectively. From such data at

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<sup>(6)</sup> Herzberg, G. Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules; Van Nostrand: Princeton, NJ, 1945.

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Figure 1. Theoretical relative population of the rotational states as a function of rotational energy in  $NO_2$  molecules at 298 K.



**Figure 2.** Fraction  $(X_{rot})$  of the NO<sub>2</sub> molecules which have rotational energies greater than  $E_{min}$  (cm<sup>-1</sup>). Curves a-i correspond to temperatures of 223, 273, 298, 325, 347, 370, 398, 496, and 566 K, respectively.

each temperature we have calculated the fraction of molecules having energies greater than 422 cm<sup>-1</sup>, the energy deficiency for NO<sub>2</sub> photodissociation at 404.7 nm. These fractions (summarized in Table I, column 2) should be compared with the observed  $\phi_1$ values (column 7, Table I). As observed by Lee and Uselman,<sup>2</sup> Jones and Bayes,<sup>3</sup> and Gardner et al.,<sup>4</sup> we find that they are much too small to account for the fraction of NO<sub>2</sub> molecules dissociating even if all of the rotational energy were available for dissociation. There must be some unidentified problem in the earlier calculations of Pitts et al.<sup>1</sup> which showed quantitative agreement between experimental  $\phi_1$  values and simple theory based upon rotational energy alone.

The fraction of molecules of NO<sub>2</sub> which possess at least one quantum of vibrational energy can be calculated readily from the function  $1 - X_0$ , where  $X_0$ , the fraction of the molecules in the v = 0 level, is given by

$$X_0 = [1 - \exp(-\nu_1/\Theta)][1 - \exp(-\nu_2/\Theta)][1 - \exp(-\nu_3/\Theta)]$$

 $v_1$ ,  $v_2$ , and  $v_3$  are the fundamental vibrational frequencies (cm<sup>-1</sup>) of the NO<sub>2</sub> molecule (1319.7, 749.8, and 1617.75, respectively), and  $\theta$  is equal to 0.6950*T* (cm<sup>-1</sup>). Of course vibration in the lowest energy mode  $v_2$  with v = 1 is the favored excitation at the lower temperatures, but excitation in the other modes and overtones becomes significant at the higher temperatures; thus, at 566 K 35% of the vibrational excitation is in modes other than  $v_2$  with v = 1. However, the fraction of the molecules which contain at least one quantum of vibrational excitation,  $(1 - X_0)$  in column 3 of Table I, is relatively small at all of the temperatures at which



Figure 3. Plot of the function  $\sigma_{obs}/X_0$  versus  $(1 - X_0)/X_0$ , where  $\sigma_{obs}$  is the observed cross section of NO<sub>2</sub> in the 404.7-nm region and  $X_0$  is the theoretical fraction of NO<sub>2</sub> molecules which are vibrationless at the given temperature. The  $\sigma_{obs}$  data were determined in experiments at temperatures from 273 to 370 K. From the intercept and the slope of the least-squares line shown, values of the cross sections for vibrationless and vibrationally excited NO<sub>2</sub>, respectively, are derived.

NO<sub>2</sub> photodissociation has been studied (223-566 K). If we assume that at 404.7 nm the absorption cross section of a vibrationally excited NO<sub>2</sub> molecule ( $\sigma_v$ ) is about the same as that for a vibrationless molecule of NO<sub>2</sub> ( $\sigma_0$ ), then vibration energy can contribute little to the enhanced quantum yield of NO<sub>2</sub> photodissociation at ordinary temperatures.

However, if for 404.7-nm light  $\sigma_v$  is larger than  $\sigma_0$ , then obviously a more significant fraction of the dissociation can result from vibrationally excited NO<sub>2</sub> molecules. It is possible that the increase in the observed  $\sigma$  for NO<sub>2</sub> at 404.7 nm with increase in temperature is a consequence of  $\sigma_v > \sigma_0$ , and if so, then vibrational contributions to  $\phi_1$  may be important. To test this hypothesis, we may attempt to derive the values of  $\sigma_v$  and  $\sigma_0$  from our cross section data and then calculate the possible influence of vibrational excitation in NO<sub>2</sub> photodissociation for  $\lambda > 397.9$  nm. According to this simple hypothesis the observed cross section ( $\sigma_{obs}$ ) for NO<sub>2</sub> at a given temperature is given by the relation

$$\sigma_{\rm obs} = X_0 \sigma_0 + (1 - X_0) \sigma_{\rm v}$$

Thus, a plot of  $\sigma_{obs}/X_0$  versus  $(1 - X_0)/X_0$  should be a straight line with a slope equal to  $\sigma_v$  and intercept equal to  $\sigma_0$ . Such a plot is shown in Figure 3. From the slope and intercept we derive the estimates  $\sigma_0 = (5.46 \pm 0.36) \times 10^{-19}$  and  $\sigma_v = (2.51 \pm 0.78)$  $\times$  10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup>. (Error limits shown are twice the standard deviation.) The data follow the theoretically expected linear form reasonably well and appear to support the hypothesis of vibrationally excited NO<sub>2</sub> involvement in absorption of light in the 404.7-nm region. The large difference between  $\sigma_0$  and  $\sigma_v$  at 404.7 nm suggested by these results is somewhat surprising at first sight. One expects that the integrated intensity of the first electronic absorption band of NO2 which originates from the ground-state  $NO_2(v=0)$  to the manifold of excited states will be qualitatively similar to the corresponding band originating with  $NO_2(v>0)$ . However, a shift in absorption onset to lower energies (>749.8 cm<sup>-1</sup>) and a shift in vibrational structure are expected for the  $NO_2(v>0)$  band. If the oscillations in the vibrational structure of the bands are out of phase so that a maximum in the  $\sigma_v$  occurs near 404.7 nm while a minimum in the  $\sigma_0$  band occurs at 404.7 nm, then in principle one might account for the relatively large difference which we suggest between  $\sigma_0$  and  $\sigma_v$  at 404.7 nm.

The energy deficiency for dissociation of an NO<sub>2</sub> molecule excited at 404.7 nm is 422 cm<sup>-1</sup>. Thus, a molecule of NO<sub>2</sub> which contains at least one quantum of vibrational energy and absorbs a photon of 404.7-nm light will possess enough energy to dissociate regardless of its rotational excitation. We will assume that such a molecule will dissociate with a quantum yield of unity. NO<sub>2</sub> molecules which absorb a quantum of  $\lambda < 392.8$  nm, the energy equivalent to a vibrationally excited NO<sub>2</sub>( $\nu_2, \nu=1$ ) which absorbs a 404.7-nm quantum, dissociate with  $\phi_1 > 0.95.^4$  From the estimates of the cross sections for the vibrationless and vibrationally excited NO<sub>2</sub> molecules, we can estimate the fraction of the total 404.7-nm light-absorbing molecules which are in the vibrationally excited states at each temperature  $(\phi_{vib})$  using the following relation:

$$\phi_{\rm vib} = \sigma_{\rm v} (1 - X_0) / [(1 - X_0)\sigma_{\rm v} + X_0\sigma_0]$$

These fractions ( $\phi_{vib}$ ), shown in column 4 of Table I, may in theory contribute directly to the observed  $\phi_1$  values. In addition, the remaining fraction of the light-absorbing molecules  $(1 - \phi_{vib})$  which have rotational energies greater than 422 cm<sup>-1</sup>, given by

$$\phi_{\rm rot} = (1 - \phi_{\rm vib})(X_{\rm rot})$$

may contribute (column 5, Table I). The theoretical values for  $\phi_1$  (equal to  $\phi_{vib} + \phi_{rot}$ ) may be compared with the experimental values for  $\phi_1$  in Table I, columns 6 and 7, respectively. It is clear that there is reasonable agreement between the theory and experiment for data over a wide temperature range. The results from the lowest (223 K) and highest temperatures (566 K) which show the largest differences are least reliable because of experimental difficulties. Davenport's measurements of  $\phi_1$  at 223 K<sup>8</sup>

were very difficult and probably inaccurate; the results of Pitts et al.<sup>1</sup> at 566 K required a significant correction for the thermal decomposition of  $NO_2$ .

### Conclusion

We conclude from the present considerations that vibrationally excited NO<sub>2</sub> molecules absorb 404.7-nm light more strongly than vibrationally unexcited NO<sub>2</sub>, and the photodecomposition of these molecules can account for the "missing" fraction of 404.7-nm excited NO<sub>2</sub> molecules which had previously appeared to possess insufficient electronic plus internal energy to decompose.

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# Why Energy Embedding Works

## G. M. Crippen

College of Pharmacy, University of Michigan, Ann Arbor, Michigan 48109 (Received: September 17, 1987)

Energy embedding is a numerical technique for locating conformations of molecules corresponding to very good local minima of the potential function used, which generally has involved only atom-pair interactions. Computational experience with various molecular force fields has shown it has a remarkable talent for locating either the global energy minimum or nearly equally favorable minima, thus bypassing numerous uninteresting high-energy minima. Here it is shown that the algorithm is indeed well-defined in general, that it will directly converge to the global minimum of energy given certain reasonable properties of the potential function, and that it can be successfully applied to any standard molecular mechanics force field, such as AMBER, which includes bond angle bending and intrinsic torsional terms in addition to atom-pair interactions.

#### Introduction

The basic premise of molecular mechanics is that given an adequate approximation to the internal energy of a molecule as a function of conformation, the physically significant conformations are those which are near the lowest local minima of energy. The problem is that even for molecules having only a few rotatable bonds, there are numerous uninteresting minima lying well above the global minimum. One can either search exhaustively over all possible conformations or initiate local energy minimizations from many starting points. Neither approach is feasible for molecules having more than about six rotatable bonds.<sup>1</sup> The problem is particularly acute for predicting the conformation of globular proteins, due to their very many degrees of conformational freedom. A promising way around the problem has been "energy embedding",<sup>2,3</sup> an outgrowth of the distance geometry approach to conformational analysis.<sup>4</sup> The energy embedding algorithm basically consists of locating a very low energy conformation for the molecule in a high-dimensional space ( $\mathbb{R}^n$ , where each atom has n Cartesian coordinates) and then keeping the energy minimal subject to the gradually increasing constraint that the molecule lie in  $\mathbb{R}^3$ . To put it more picturesquely, the molecule first is allowed to pucker up into the additional dimensions to produce a generally rather compact ball having very low energy, since the atoms have more freedom to satisfy all the energy terms they are involved in. Then the molecule is gradually flattened back into three dimensions, allowing the atoms to reshuffle between the jaws of the vice (so as to maintain as low an energy as they can) after every turn of the vice handle. The exact details of how this is done are apparently rather unimportant, because variations on the original method also work satisfactorily.<sup>5,6</sup> There are two questions to be addressed: why does this procedure work at all, and will it work on the sorts of force fields which are widely used in molecular mechanics programs? The answer to the first question can best be seen by examining the simple examples in the next section, and the subsequent section shows indeed how well it works with the AMBER molecular mechanisms program.

### Simple Examples

To begin with, consider a situation so simple that it can easily be displayed in two-dimensional diagrams. Suppose we have three atoms in the plane  $\mathbb{R}^2$ , with  $a_1$  fixed at (0,0),  $a_3$  fixed at (2,0),

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