

Laser photodetachment of NO_2^- *

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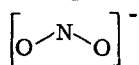
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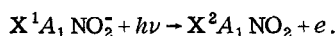
An absolute apparent cross section for the photodetachment of nitrite (NO_2^-) ions has been measured in the region (2.0–2.7) eV utilizing a tunable dye laser as the light source. The electron affinity of nitrogen dioxide (NO_2) has been determined to be (2.36 ± 0.10) eV. Photodetachment of an ion thought to be a peroxy isomer of NO_2^- has also been observed.

I. INTRODUCTION

The tunable laser photodetachment method has been very productive in determining electron affinities and photodetachment cross sections for a variety of atomic species.^{1,2} Recently, the method has been utilized to study the diatomic ion OH^- .³ This paper reports a tunable laser photodetachment study of the nitrite ion (labelled NO_2^-) of molecular geometry

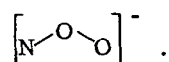


The particular process studied is



The dependence on photon energy of the absolute (ion temperature-dependent) apparent cross section is measured in the vicinity of the NO_2^- photodetachment onset (2.0–2.65) eV at an ion temperature $T \approx 1500$ – 2000 °K. By theoretical reproduction of the observed spectrum, we are able to deduce a value of (2.36 ± 0.10) eV for the electron affinity of nitrogen dioxide (NO_2). The apparent cross section for NO_2^- photodetachment is a strong function of ion temperature in the energy region studied. Our analysis permits estimation of this quantity at other temperatures, including specifically temperatures that pertain in the atmospheric *D* region.

In addition to NO_2^- , photodetachment of another ion of $m/e = 46$ is observed. This unusual ion, labelled NO_2^* , is probably a peroxy isomer of NO_2^- ,⁴ of molecular geometry



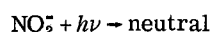
II. EXPERIMENTAL

The apparatus and data analysis used in this work have been fully described previously.¹ A 2.5 keV beam of negative ions is extracted from a hot cathode plasma ion source at estimated temperature $T \approx 1500$ – 2000 °K, mass analyzed as $m/e = 46$, and intersected by radiation from a pulsed flashlamp-pumped, tunable dye laser of ~ 1 Å bandwidth. Ion currents, typically ≥ 100 nA, are detected on a Faraday cup. Photodetached neutrals strike the cathode of a multiplier and are detected by the resultant electron current. Analysis of the data yields an apparent cross section (σ'_{app}) as a function of photon energy *E* given by the formula

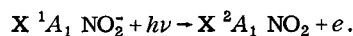
$$\sigma'_{\text{app}}(E) = \sum_{k=1}^{200} \frac{[NS(k) - NB(k)] - LEN}{[IS(k)][LS(k)]}, \quad (1)$$

where *k* represents the *k*th laser firing ($1 \leq k \leq 200$) at a given frequency, *NS(k)* is the neutral signal (photodetached and charge-stripped on the background gas) on the *k*th firing, *NB(k)* is the neutral signal (charge-stripped) just prior to the *k*th firing, *IS(k)* is the ion beam current during the *k*th firing, *LS(k)* is the laser flux at the *k*th firing, and *LEN* is the laser electrical noise induced in the neutral detector. The measured relative cross section σ'_{app} , accurate to $\pm 10\%$, is in general the sum of cross sections for photodetachment and photodissociation. An absolute apparent cross section (labelled σ_{app}) is obtained by comparison with the known absolute cross section for O^- photodetachment.^{1,5} Corrections must be made for the difference in multiplier gain between O atoms and the particular neutrals being formed (e.g., NO_2) as well as for the different velocities of iso-energetic O^- and NO_2^- ions which result in different times spent in the intersection with the laser beam.

In this experiment, ions are produced in the plasma source from two neutral gaseous precursors. The first gas utilized is O_2 and a trace of N_2 . Photon bombardment of the ion beam at $m/e = 46$ reveals two distinct ionic species, one of which produces neutrals when intersected with photons of energy ≥ 1.8 eV while the other requires photons of energy ≥ 2.2 eV. Variation of the source parameters allows good selection of one ion or the other. Nitrogen dioxide, the other gas used, forms only that ion which produces neutrals upon interaction with photons of energy ≥ 2.2 eV. This ion must clearly be NO_2^- because the electron affinity of NO_2 has been measured by a variety of techniques to be (2.4 ± 0.2) eV.^{6–8} The process measured



is undoubtedly completely photodetachment since the lowest energy photodissociation channel does not open until ≈ 4 eV. The photodetachment process involves the ground electronic states of both NO_2^- and NO_2 :



The other ion, labelled NO_2^* , is thought to be a peroxy isomer of NO_2^- (see Sec. V). Upon interaction with photons of energy ≥ 1.8 eV, it photodetaches via the probable mechanism



The absolute cross sections (σ_{app}) for NO_2^- and NO_2^* photodetachment determined by the approach outlined above are presented in Fig. 1. The absolute cross sec-

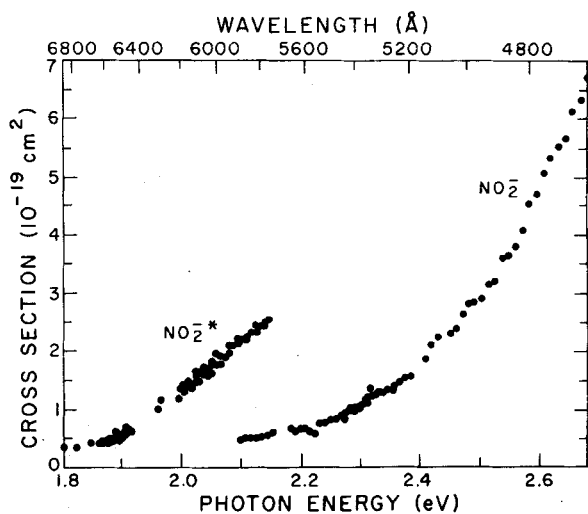
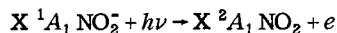


FIG. 1. Apparent cross sections for photodetachment of NO_2^* and NO_2^- in the region (1.8–2.7) eV. Although the relative cross sectional values have been measured to an accuracy of 10%, the absolute values are known only to $\pm 40\%$.

tion scale shown is accurate to $\pm 40\%$ for NO_2^- . When the O_2 source is utilized, it is unclear whether variation of the source parameters allows *total* selection of NO_2^- or NO_2^* . If the NO_2^* beam contains a small percentage of NO_2^- , the σ_{app} for NO_2^* photodetachment determined by our approach is too low because NO_2^- has a much smaller cross section for photodetachment than does NO_2^* at the energies involved (1.8–2.2 eV). [See Expression (1).] Thus, within the $\pm 40\%$ error bounds, the absolute NO_2^* cross section shown in Fig. 1 is a lower bound to the true cross section. The data labelled NO_2^- in Fig. 1 are obtained using NO_2 as the gas in the ion source.

III. SIMULATION OF NO_2^- PHOTODETACHMENT SPECTRUM

The photodetachment process



consists of numerous transitions from vibrational states i of $^1A_1 \text{NO}_2^-$ to such states j of $^2A_1 \text{NO}_2$.⁹ Each of these transitions has a cross-sectional dependence on energy in the threshold region that is not well understood. For a $p\pi$ electron departing a molecule with a permanent dipole moment, this dependence is probably between a step function and a square root function.³ In this work it is assumed that¹⁰

$$\sigma_{ij}(E - E_{ij}) = \sigma^0 |I_{ij}|^2 (E - E_{ij})^{1/4}, \quad (2)$$

where σ_{ij} is the cross section for the $i \rightarrow j$ channel with threshold energy E_{ij} (cm^{-1}), $E \geq E_{ij}$ is the photon energy, I_{ij} the vibrational overlap integral between states i and j , and σ^0 a multiplicative factor. The threshold energy is given by the expression

$$E_{ij} = EA(\text{NO}_2) + E_j - E_i, \quad (3)$$

where E_j , E_i are the energies of states j , i relative to the ground vibrational levels of the respective electronic states and $EA(\text{NO}_2)$, the NO_2 electron affinity, is defined

as the energy separation between the ground vibrational levels. The apparent total cross section, which is the quantity measured in this experiment, can be obtained from the expression

$$\sigma_{\text{app}}(E) = \sum_{i,j} \sigma_{ij}(E - E_{ij}) N_i / \sum_i N_i, \quad (4)$$

where N_i is the density of NO_2^- molecules in state i . If the NO_2^- vibrational distribution is assumed to be Boltzmann, then the factor $N_i / \sum_i N_i$ reduces to a Boltzmann factor. The summation over j levels in expression (4) is restricted to those channels for which $E_{ij} \leq E$.

The calculation of Franck-Condon factors ($|I_{ij}|^2$) is necessary to obtain σ_{app} . Both $^1A_1 \text{NO}_2^-$ and $^2A_1 \text{NO}_2$ are nonlinear molecules of symmetry C_{2v} and possess three normal modes of vibration— $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(B_2)$ —labelled the symmetric stretch, bend, and asymmetric stretch respectively.¹¹ Table I lists the frequency of these modes as well as additional information concerning the ground electronic states of NO_2^- and NO_2 . The NO_2^- vibrational data are gathered from condensed phase studies of nitrite ions in interactive environments and are only approximately correct for the free gas phase species. A recent infrared study of NO_2^- in a noninteracting argon matrix has yielded an asymmetric stretching frequency of 1244 cm^{-1} which is in good agreement with the value used in this work.¹²

The overlap integral I is given by the formula

$$I(\nu'_1 \nu'_2 \nu'_3 - \nu_1 \nu_2 \nu_3) = \int \int \int \psi_{\nu'_1 \nu'_2 \nu'_3}^* (Q'_1 Q'_2 Q'_3) \times \psi_{\nu_1 \nu_2 \nu_3} (Q_1 Q_2 Q_3) dQ_1 dQ_2 dQ_3. \quad (5)$$

Unprimed variables represent NO_2^- whereas primed variables represent NO_2 . The vibrational wavefunctions are functions of the normal coordinates Q_i , Q'_i ($i=1, 2, 3$) with quantum numbers ν_i , ν'_i ($i=1, 2, 3$) and, in the harmonic approximation, are products of one-dimensional harmonic oscillator functions.¹¹ The integral is arbitrarily taken over NO_2^- coordinates. To integrate (5), it is necessary to express the NO_2 normal coordinates Q' in terms of the NO_2^- coordinates Q :

TABLE I. Parameters of $\text{NO}_2^- (^1A_1)$ and $\text{NO}_2 (^2A_1)$.

| | NO_2^- | NO_2 |
|--|--------------------|----------------------|
| ν_1 (cm^{-1}) | 1332 ^a | 1320 ^b |
| ν_2 (cm^{-1}) | 821 ^a | 750 ^b |
| ν_3 (cm^{-1}) | 1240 ^a | 1617.75 ^b |
| $d(\text{N}-\text{O})$ (\AA) | 1.236 ^c | 1.1934 ^d |
| α ($\angle \text{O}-\text{N}-\text{O}$) | 115.4 ^c | 134.1 ^d |
| f_{11} ($\text{mdyn}/\text{\AA}$) | 9.85 ^a | 12.43 ^b |
| f_{α}/d^2 ($\text{mdyn}/\text{\AA}$) | 1.7 ^a | 1.0968 ^b |
| $f_{\alpha d}/d$ ($\text{mdyn}/\text{\AA}$) | 0.505 ^a | 0.535 ^b |

^aThese are averaged from NaNO_2 (aqueous) data. See R. E. Weston, Jr. and T. F. Brodasky, *J. Chem. Phys.* **27**, 683 (1957).

^bE. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.* **2**, 413 (1958) (fundamental data).

^cG. V. Pfeiffer and L. C. Allen, *J. Chem. Phys.* **51**, 190 (1969).

^dG. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl, Jr., A. C. Kunkle, J. W. Bransford, J. Rastrup-Andersen, and J. Rosenthal, *J. Chem. Phys.* **16**, 442 (1948).

TABLE II. Calculated Franck-Condon factors for the transition $^* \cdot h\nu + X^1A_1NO_2(0, v_2, 0) \rightarrow X^2A_1 NO_2(0, v_2', 0) + e$.

| $v_2 \dagger$ | $v_2' \rightarrow$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|---------------|--------------------|--------|--------|--------|--------|--------|--------|--------|
| 0 | | 0.0026 | 0.0149 | 0.0315 | 0.0793 | 0.1077 | 0.1139 | 0.1162 |
| 1 | | 0.0088 | 0.0322 | 0.0359 | 0.0343 | 0.0061 | 0.0043 | 0.0217 |
| 2 | | 0.0113 | 0.0226 | 0.0083 | 0.0001 | 0.0146 | 0.0290 | 0.0050 |
| 3 | | 0.0179 | 0.0153 | 0.0000 | 0.0150 | 0.0198 | 0.0018 | 0.0302 |
| 4 | | 0.0156 | 0.0031 | 0.0047 | 0.0134 | 0.0003 | 0.0115 | 0.0432 |
| 5 | | 0.0106 | 0.0000 | 0.0072 | 0.0018 | 0.0066 | 0.0113 | 0.0039 |
| 6 | | 0.0107 | 0.0010 | 0.0013 | 0.0344 | 0.0770 | 0.0416 | 0.0187 |

[†]Harmonic approximation.

$$Q' = JQ + K \quad (6)$$

It can be shown that the orthogonal matrix **J** connects only those normal modes of the same symmetry and that **K** has nonzero elements only for totally symmetric (A_1) modes.^{13,14} As a result, Eq. (5) simplifies to

$$I(v_1' v_2' v_3' - v_1 v_2 v_3) = \int \int \psi_{v_1}^* \cdot (Q_1') \psi_{v_2}^* \cdot (Q_2') \psi_{v_1}(Q_1) \psi_{v_2}(Q_2) dQ_1 dQ_2 \\ \times \int \psi_{v_3}^*(Q_3) \psi_{v_3}(Q_3) dQ_3. \quad (7)$$

The single integral in the $Q_3(B_2)$ coordinate is easily ascertained. For a mode of symmetry other than A_1 , the only nonzero overlap integrals are those involving transitions of zero or an even number of quanta.¹⁵ Use of Ansbacher's¹⁶ analytical expression for the harmonic oscillator overlap integral reveals that in this instance $\Delta v_3 = \pm 2, \pm 4, \dots$ transitions have less than 1% of the intensity of diagonal transitions and are ignored. The four $v_3' - v_3$ transitions considered are 0-0, 1-1, 2-2, 3-3; their overlap integrals are nearly unity.

Evaluation of the double integral in (5) involving the two A_1 coordinates requires a knowledge of **J** and **K**. The prerequisite matrix elements are obtained by standard solutions of the vibrational eigenvalue problem to yield^{11,13,14}

$$Q_1' \approx 0.95 Q_1 - 0.31 Q_2 + 2.08 \times 10^{-21} (g^{1/2} - \text{cm}) \\ Q_2' \approx 0.31 Q_1 + 0.95 Q_2 + 8.55 \times 10^{-21}. \quad (8)$$

Since the O-N-O angle in NO₂ is $\approx 19^\circ$ larger than in NO₂⁻ (Table I), it is expected that overlap integrals involving the bending mode will be quite off-diagonal. The N-O internuclear distance does not vary greatly from NO₂ to NO₂⁻, but the symmetric stretch normal mode has a sufficient amount of "bend" so that overlap integrals involving this coordinate are also expected to be somewhat off-diagonal. The double integral is computed numerically for 49 bending transitions involving the levels $0 \leq v_2 \leq 6$ and $0 \leq v_2' \leq 6$ for the symmetric stretch transitions ($v_1' - v_1$): 0, 1, 2-0; 0, 1, 2, 3-1; 0, 1, 2, 3, 4-2; 0, 1, 2, 3-3.

We are now able to compute the Franck-Condon factors for most of the transitions occurring in the vicinity ($\pm 3000 \text{ cm}^{-1}$) of the NO₂⁻ photodetachment onset [$E \sim EA(\text{NO}_2)$] and originating from vibrational levels within 4500 cm^{-1} of the ground NO₂⁻ level. As examples, the Franck-Condon factors for the transitions $0v_2'0 - 0v_20$ are listed in Table II.

To simulate the experimental photodetachment spectrum, it is necessary to estimate the source temperature T . One then varies the unknown parameters— σ^0 and $EA(\text{NO}_2)$ —until a satisfactory fit is obtained between the calculated curve of σ_{app} vs E , determined by expressions (2)–(4), and the experimental spectrum. The estimated source vibrational temperature is in the range $1500^\circ\text{K} \leq T \leq 2000^\circ\text{K}$. Figure 2 depicts the best fit to the experimental data at 1500°K . By varying such parameters as the ion "temperature," and the form of the threshold law, we arrive at the conclusion

$$EA(\text{NO}_2) = (2.36 \pm 0.10) \text{ eV}.$$

The principal source of error in this determination lies in the applicability of the model. If both the threshold law and a true ion temperature were known, then we could obtain a fit accurate to $\pm 0.01 \text{ eV}$. In fact we must vary the NO₂⁻ vibrational distribution and the threshold law to determine the sensitivity of $EA(\text{NO}_2)$ to variations in these essentially unknown quantities. It is these variations which give rise to the quoted $\pm 0.10 \text{ eV}$ uncertainty. Thus changing the threshold law from E^0 to $E^{1/2}$ gives rise to a $\pm 0.05 \text{ eV}$ uncertainty, although neither of these limiting cases is expected, and the quality of the fit obtained is poorer than in the case of the $E^{1/4}$ law actually adopted. Other such contributions include correlation with the scale parameter σ^0 ($\pm 0.03 \text{ eV}$), uncertainty in the ion source "temperature" ($\pm 0.03 \text{ eV}$), and neglect of rotational effects ($\pm 0.01 \text{ eV}$). Our reported error of $\pm 0.10 \text{ eV}$ for $EA(\text{NO}_2)$ is our best estimate of the combined effects of these several error sources.

The NO₂⁻ photodetachment cross section is of interest in D -region chemistry. Utilizing values of σ^0 and $EA(\text{NO}_2)$ obtained from a fit to the data at $T \approx 1750^\circ\text{K}$, we are able to estimate σ_{app} vs E in the onset region [$E \sim EA(\text{NO}_2)$] at $T = 250^\circ\text{K}$, a relevant atmospheric temperature. This is shown in Fig. 3. It should be noted that σ_{app} is a strong function of temperature only in the vicinity of $E \sim EA(\text{NO}_2)$ where relatively few channels are open among accessible levels of NO₂⁻.

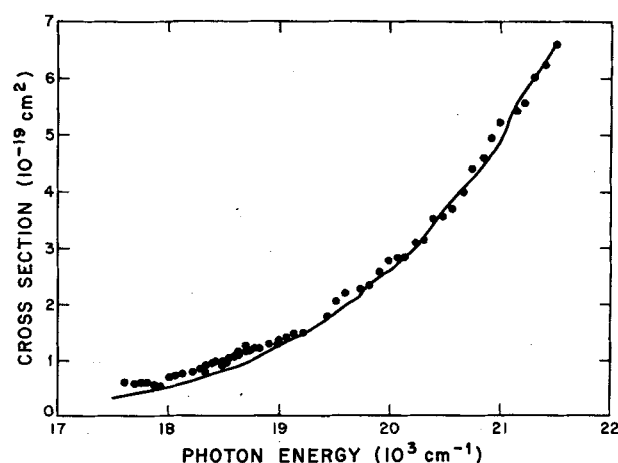


FIG. 2. Observed and simulated apparent cross sections for NO₂⁻ photodetachment in the region $17\,500\text{--}21\,500 \text{ cm}^{-1}$ ($2.17\text{--}2.67 \text{ eV}$). The points represent experimentally determined values while the line represents the best fit to the data at $T = 1500^\circ\text{K}$.

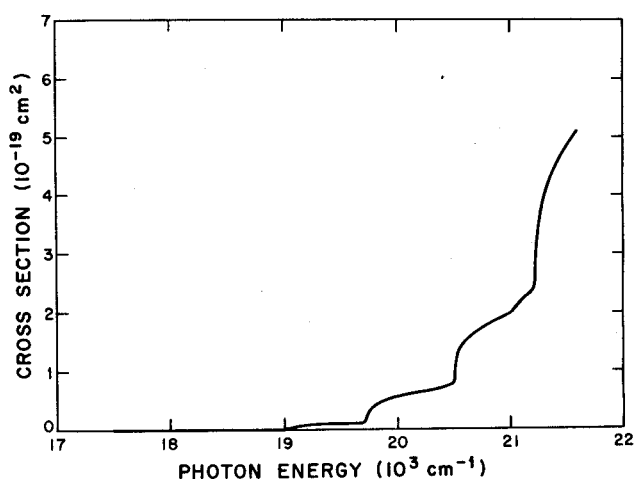


FIG. 3. Calculated apparent cross section for NO_2^- photodetachment in the region $17\,500\text{--}21\,500\text{ cm}^{-1}$ ($2.17\text{--}2.67\text{ eV}$) at $T=250\text{ K}$. Rotational effects, which would broaden the sharp discontinuities in the curves, are not included.

IV. DISCUSSION OF NO_2 ELECTRON AFFINITY

The NO_2 electron affinity determined by tunable laser photodetachment is at least 0.4 eV lower than the lowest affinity determined by photodetachment studies using conventional light sources.^{4,17} The reason for this difference is that the Franck-Condon factors for the photodetachment transition are quite off diagonal. [The transition $\text{NO}_2^-(0, 0, 0) \rightarrow \text{NO}_2(0, 0, 0)$ has a Franck-Condon factor of 0.003 .] The advantage of laser photodetachment in this case lies in the intensity of radiation available in a narrow bandwidth which permits measurement of absolute cross sections as small as $2\text{--}3 \times 10^{-20}\text{ cm}^2$.

The electron affinity reported here is in excellent agreement with charge-transfer studies. Dunkin *et al.*⁶ report a value of $(2.38 \pm 0.06)\text{ eV}$ whereas Hughes *et al.*⁷ report a value of $(2.28 \pm 0.10)\text{ eV}$. Charge transfer studies rely, however, on knowledge of the electron affinities of other species while laser photodetachment has no such handicap.

To confirm the reliability of our theoretical analysis, we have examined the recent NO_2^- photodetachment study of Richardson *et al.*⁴ These authors produced NO_2^- at room temperature in an ion cyclotron apparatus and photodetached the ion with conventional light sources of bandwidth ± 0.2 and $\pm 0.4\text{ eV}$. If we utilize our calculated σ_{app} vs E curve at $T=250\text{ K}$ (Fig. 3) and convolute σ_{app} with an appropriate spectral resolution function, we are able to reproduce approximately the long wavelength edge of the NO_2^- photodetachment spectrum of Richardson *et al.*⁴

The tunable laser photodetachment method can be utilized to determine the affinities of a wide variety of molecules provided that there is some knowledge of the valence force constants of both the neutral species and the negative ion. Otherwise, fixed frequency laser photoelectron spectroscopy may be preferable.¹⁸

V. NO_2^*

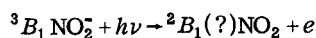
The unusual ion of $m/e=46$ produced in our plasma source by electron bombardment of O_2 (in the presence of trace amounts of N_2) has been designated NO_2^* . There are three reasonable choices for the identity of NO_2^* :

- (1) a highly excited set of vibrational levels of $X\ ^1A_1\ \text{NO}_2^-$;
- (2) an excited metastable triplet state of NO_2^- ;
- (3) a peroxy isomer of NO_2^- .

By the third possibility, we mean specifically that the potential surface for the ground state of NO_2^- has a second minimum at internuclear distances quite distinct from those of ordinary NO_2^- .

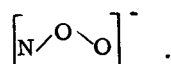
The possibility that NO_2^* is vibrationally excited $^1A_1\ \text{NO}_2^-$ is a remote one. If the plasma source is roughly in thermal equilibrium vibrationally, our Franck-Condon analysis predicts a minimum temperature of 5000 K necessary to simulate the onset of the NO_2^* photodetachment spectrum. It is unreasonable to assume that the minor change in source parameters which results in NO_2^* production rather than NO_2^- production can triple the estimated vibrational temperature. There is no previous evidence for such a high vibrational temperature.

The lowest reported triplet state of NO_2^- , of 3B_1 symmetry, has its ground vibrational level $18\,959\text{ cm}^{-1}$ above the 1A_1 state.¹⁹ This level lies less than 100 cm^{-1} below the ground state of NO_2 and is the only vibrational level of the 3B_1 state stable with respect to "autodetachment" into $\text{NO}_2 + e$.²⁰ The onset of the process¹⁵

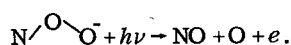


occurs at $\leq 1.9\text{ eV}$ in agreement with the observed NO_2^* photodetachment onset. It is difficult, however, to imagine efficient production of such a fragile and highly energetic metastable in our source. An additional argument against possibilities (1) and (2) is the observation by Richardson *et al.*⁴ of an anomalous form of NO_2^- existing in an ion cyclotron trap on the order of seconds.

We are left with the third possibility; namely, that NO_2^* is a peroxy isomer of NO_2^- of probable electronic structure



This possibility is strengthened by the existence of the isoelectronic N-O-F .²¹ Previous investigators^{4,22} have reported evidence for a peroxy form of NO_2^- . In addition, strong evidence exists for a peroxy form of the ion NO_3^- (O-O-N-O^-).²³ Let us assume that the oxygen-oxygen bond in NO_2^* is a weak electrostatic interaction between NO and O^- . Then, the photodetachment process is probably

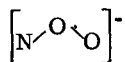


An approximate onset for this process can be obtained from the expression

$$E_{\text{onset}} \approx EA(\text{O}^-) + \bar{E}(T),$$

where \bar{E} is the average bond energy between NO and O^-

at temperature T . If the $\text{NO} \cdots \text{O}^-$ bond were partly electrostatic, a reasonable estimate for $\bar{E}(T \approx 1500 \text{ }^\circ\text{K})$ would be $\approx 0.5 \text{ eV}$.²⁴ Then, since $EA(\text{O}^-) = 1.46 \text{ eV}$,²⁵ $E_{\text{onset}} \approx (1.9 - 2.0) \text{ eV}$, in reasonable agreement with observation (Fig. 1). To prove the existence of



more rigorously, a laser photoelectron study should be undertaken.¹⁸

VI. SUMMARY

We have measured the absolute apparent cross section (σ_{app}) for NO_2^- photodetachment to an accuracy of $\approx 40\%$ in the region (2.0–2.7) eV. The use of a pulsed, tunable dye laser has permitted observation of cross sections as small as $2 \times 10^{-20} \text{ cm}^2$. Through simulation of the observed spectrum, the electron affinity of nitrogen dioxide has been determined to be $(2.36 \pm 0.10) \text{ eV}$. In addition, we have measured σ_{app} for a second ion with $m/e = 46$, labelled NO_2^* , in the region (1.8–2.2) eV. The most reasonable explanation of this second spectrum is that it is caused by photodetachment of a peroxy isomer of NO_2^- .

Note added in proof: In an article to be published in *J. Am. Chem. Soc.*, P. Pearson *et al.* calculate that a peroxy isomer of NO_2^- exists and that there is a high potential barrier which inhibits conversion of $[\text{N}-\text{O}-\text{O}]^-$ to the more stable isomer. This calculation reinforces our conclusion that the two distinct photodetachment spectra observed are caused by $[\text{N}-\text{O}-\text{O}]^-$ and $[\text{O}-\text{N}-\text{O}]^-$, respectively.

ACKNOWLEDGMENTS

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†Alfred P. Sloan Foundation Fellow, 1972–74.

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⁹Rotational levels are too closely spaced to be included in this treatment.

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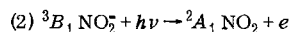
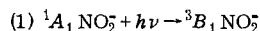
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