A multiphoton ionization study of the photodissociation dynamics of the $S_2$ state of CH$_3$ONO

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Two-color $(1+1)$ REMPI (resonantly enhanced multiphoton ionization) photoelectron spectroscopy is used to probe the NO photofragments produced by the UV photodissociation of methyl nitrite, i.e., CH$_3$ONO $+ \hbar \nu \rightarrow$ CH$_3$ONO$^*$($S_2$) $\rightarrow$ CH$_3$O$^*$($X$) + NO($X$, $v$, $J$). The photofragments are produced in their ground electronic states but with high rotational and translational energy. NO fragment angular distributions, rotational state distributions, and spatial alignment are determined by photoion and photoelectron detection. The initial state alignment is obtained by the CDAD (circularly dichroic angular distribution) technique for the first time. CDAD measurements for rotational levels with $35.5 < J < 46.5$ result in alignment parameters at the classical high-$J$ limit of $a_0^{(2)} = -0.4$. This alignment is consistent with an "impulsive" dissociation mechanism in which photofragment recoil along the CH$_3$O–NO bond imparts substantial rotational angular momentum to the NO molecule resulting in a high-J state distribution and preferential rotation in the plane of dissociation. These measurements clearly establish the utility of the CDAD method for probing chemical processes in which spatial alignment plays an important role. Photoion angular distributions are used to probe correlations between the CH$_3$ONO transition dipole moment, NO fragment velocity, and angular momentum. These correlations reveal additional details of the photolysis mechanism.

I. INTRODUCTION

Photodissociation processes which yield NO as a fragment have been the subject of numerous investigations. The NO fragment has been chosen for detailed study on the basis of its well defined spectroscopy and the accessibility of its excited states with current laser technology. A number of groups have been conducting detailed studies of several representative molecules, such as: nitrous acid, HONO,$^2$,$^3$ methyl nitrite, CH$_3$ONO,$^4$–$^{13}$ ethyl nitrite,$^{14}$,$^{15}$ and t-butyl nitrite, (CH$_3$)$_3$CONO.$^{16}$,$^{17}$ These studies have probed the angular distributions, vibrational and rotational energy distributions, and alignment of the NO product fragment. The dissociation was achieved by exciting either of two lowest states common to all of the abovementioned species. The $S_1$ state is characterized by a structured $\pi^* \rightarrow \pi$ band in the range 300–380 nm; only vibrational structure is clearly discernible, suggesting that this is a short-lived predissociative state. The $S_2$ state is associated with a structureless broad $\pi^* \rightarrow \pi$ absorption band in the range 180–250 nm, characteristic of a purely repulsive state. For both of these dissociation channels the NO is produced in its lowest electronic state ($X^2\Sigma^+$), with small vibrational excitation and high rotational and translational energy. Since the $S_1$ and $S_2$ states appear to involve very different dissociation mechanisms, investigations of the alkyl nitrites are extremely useful for probing a wide range of dynamical interactions responsible for the dissociation of polyatomic molecules.

The predominant tool used to probe detailed dynamics of dissociation is laser induced fluorescence (LIF) with Doppler line shape analysis.$^{18}$–$^{20}$ The line shape and intensity are a function of the velocity and alignment of the photofragment, as well as the angular correlation between the angular momentum, the dissociation dipole moment, and velocity vectors. Variations in geometrical arrangement of dissociation and excitation lasers and fluorescence detector selectively bring out these dynamical features. The requirement for probing fragments with LIF is that the fragment have a significant fluorescence signal, a condition which cannot be realized for many molecules. Resonantly enhanced multiphoton ionization (REMPI) is generally considered to provide greater sensitivity than LIF for detecting the expected low concentrations of photolysis products, in addition to...
having a wider applicability\textsuperscript{21,22}. Theoretical formulations have been developed that permit extraction of alignment information from REMPI data, independently of the ionization dynamics\textsuperscript{23–28}. Recently, experimental verification of this technique has been made in the analysis of photon-induced alignment of free NO\textsuperscript{29}. In these experiments circularly dichroic angular distributions (CDAD) of photoelectrons are measured and the alignment is extracted by way of relatively simple mathematical relations. Application of the CDAD technique to the determination of ground state alignment induced by photodissociation is presented here for the first time.

The thrust of the work presented in this paper is to investigate the dissociation of the $S_2$ state of CH$_3$ONO as well as to demonstrate the utility of the CDAD technique\textsuperscript{23–28} in photodissociation studies. As part of this endeavor, we also introduce a method for analysis of vector correlations in photodissociation by measuring the angular distribution of REMPI photoions.

II. EXPERIMENTAL

Photoelectron angular distribution, dissociation product angular distribution, and rotational state population distribution measurements were performed on a photoelectron spectrometer system which has been described in previous publications\textsuperscript{29,30}. The system consists of a time-of-flight photoelectron/ion spectrometer in a vacuum chamber, and pulsed laser light sources of dissociation, excitation, and probe radiation. The time-of-flight spectrometer samples electrons or ions along an axis which is perpendicular to an axis defined by two windows in the vacuum chamber. One of the windows admits tunable linearly polarized laser radiation; the polarization vector is rotated with a Soleil–Babinet compensator tuned to 1/2-wave retardation at the wavelength of interest. The other window admits 266 nm radiation coaxially to the tunable light. The 266 nm light can be right circularly polarized, left circularly polarized, or linearly polarized by rotating the axis of a 1/4-wave plate at an angle of 45°, −45°, or 0°, respectively, from the incoming polarization vector. Both light beams are focused through 250 mm lenses mounted on translation stages to allow adjustable beam overlap. The focus is adjusted to maximize signal to two-color (1 + 1') REMPI, and to reduce one-color (tunable light) (1 + 1') REMPI.

The laser system consists of a pulsed (20 Hz) Nd:YAG (Quanta Ray DCR-2A) laser producing IR and 532 nm light with 2–3 ns pulse widths. The 532 nm photons pump a tunable dye laser (Quanta Ray PDL-1) using an approximately 6:1 mix of R590 and R610 laser dyes (Exciton). The output of the dye laser is doubled (Quanta Ray WEX), and is then mixed with residual IR to produce tunable UV radiation in the range of 227 to 223 nm with 1.0 to 2.0 mJ/pulse. A 10% beam splitter diverts some of the 532 nm pump beam to a frequency doubling crystal which produces the 266 nm light at 5 mJ/pulse. The 266 nm light can be temporally delayed 3–30 ns by extending its path length.

The methyl nitrite is synthesized\textsuperscript{31} by slow addition of an acidic solution of nitrosylsulfuric acid (HOSO$_2$ONO) to water-diluted methanol (CH$_3$OH) under a slow flow of helium. The product is purified by trap (dry-ice-acetone bath temperature) to trap (liquid nitrogen temperature) distillation. In a dry-ice-acetone bath, the CH$_3$ONO has a vapor pressure of a several Torr; it can therefore be introduced into the vacuum chamber via an effusive inlet regulated with an automatic leak valve, to give an operating pressure 7 × 10$^{-5}$ Torr. A pulsed valve inlet was not used since decomposition and clustering were difficult to control.

Photoelectron angular distributions (CDAD) are measured for the left and right circularly polarized probe laser (266 nm) as two distinct angular spectra, in which the polarization angle (relative to the detector axis) of the tunable light is scanned from 90° to 270° in increments of 10°. The scan is repeated 16 times per spectrum with 60 laser shots per angle each time. A photodiode triggered by the tunable laser light initiates the TOF digitizer. The tunable radiation performs two functions: the dissociation of the CH$_3$ONO via the $S_2$ state and excitation of the product NO from the $X^2Π$, $v = 0$ state to the $A^2Σ^+$, $v = 0$ state. Since the $S_2$ state is very broad and featureless,\textsuperscript{32} the absorption curve of CH$_3$ONO can be regarded as being flat. The TOF photoelectron spectrum may show two (1 + 1') REMPI peaks: a fast (\approx 1.8 eV) one-color peak due to 227–223 nm ionization and a slower (\approx 0.9 eV) two-color peak due to 266 nm ionization. The two-color process is selected by integrating the slower peak for each shot of the laser; the unwanted one-color signal is also reduced to below 1% of that for the two color by adjusting the focus of both laser beams. Methyl nitrite can also be dissociated by the 266 nm light. This unwanted process was eliminated by delaying the 266 nm light relative to the 223–227 nm radiation 12 ns, permitting the CH$_3$ONO to dissociate and the product NO to be excited while the 266 nm ionizing (probe) laser is off. The delayed 266 nm pulse then ionizes these excited NO fragments but cannot directly ionize ground state NO photofragments produced by 266 nm induced fragmentation.

Wavelength spectra are collected in the magic angle PINDAD configuration (MAP—the polarization-into-detector angular distribution technique is described in Sec. III B): the 1/4-wave plate is set at 0° to yield linearly polarized 266 nm radiation, with the polarization vector along (into) the detector axis. The tunable light polarization is set at the “magic angle”, 54.7° from the detector axis. In order to reduce long term instabilities and effects of laser position drift with wavelength, spectra were collected in 0.62 nm wide regions with 20% overlap between regions. The dye laser was stepped linearly by 0.0048 nm steps of its output wavelength $\lambda_{dl}$, \textsuperscript{[the doubled and summed wavelength is $\lambda = (2/\lambda_{dl} + 1/1064)^{-1}$ nm]. The spectrum segments were concatenated using the overlap region for intersegment normalization. Along with the photoelectron signal the pulse energy was measured at each wavelength with a Joule meter (Laser Precision JRP-735). The spectra were corrected for power fluctuations; since the dye curve was relatively flat the power corrected spectra did not significantly differ from the uncorrected ones. Each spectrum was scanned once with 200 laser shots per wavelength channel. Several spectra were collected in order to ensure consistency. Heights $h$ of peaks of interest were obtained by fitting each peak to a...
Gaussian, \( P(\lambda) = h \cdot \exp[-\alpha(\lambda - \lambda_0)^2] \) (the fitted parameters were \( h, \alpha, \) and \( \lambda_0 \)). The peak heights in conjunction with Eqs. (17)-(19) were used to extract rotational populations, as will be discussed below.

Ion angular distributions were obtained with the TOF spectrometer by changing the voltage potentials on various parameters with Eqs. (43). Acceleration of \( \text{NO} \) ions in the Faraday cage flight tube. Characteristic features of the TOF spectrum are two broad peaks; the fast one corresponds to fragments initially moving in the ion studies, a repeller opposite the entrance aperture is at zero \( V \), an acceleration of \( V = 0 \) V is provided into the field-free Faraday cage flight tube. Characteristic features of the TOF spectrum are two broad peaks; the fast one corresponds to fragments initially moving into the detector prior to ionization; the slow one corresponds to fragments initially moving in the opposite direction, away from the detector. (Note that for thermal \( \text{NO} \) the TOF spectrum exhibits one sharp peak located in the region between the two broad peaks.) The angular resolution for these conditions is \( \approx 35^\circ \) (in contrast to \( \approx 2^\circ \) for the photoelectron measurements). The probe (ionizing) laser is set for linearly polarized light, the polarization vector along the detector axis. The polarization vector of the probe laser is scanned from \( 0^\circ \) to \( 180^\circ \) in increments of \( 10^\circ \). The fast TOF peak is integrated over time to generate a data point at a given angle. The scan is repeated eight times per spectrum with 60 laser shots per angle each time.

III. DATA ANALYSIS

A molecule, such as a photolysis fragment, in a rotational state \( J \) has \( 2J + 1 \) angular momenta, \( M_J \), \( = -J, -J + 1, ..., J - 1, J \). If the populations \( N_{M_J} \) of these states \( M_J \) are equal then the state is considered to be isotropic. If however, states with different \( |M_J| \) values have different populations the state is considered to be aligned. The populations can be expanded in a "spherical" basis:

\[ N_{M_J} = \sum_L A_L T^M_J, \]

where the \( A_L \) are the multipole moments of alignment. The \( T^M_J \) are known as spherical tensor operators which can be expressed as Clebsch-Gordon coefficients:

\[ T^M_J = (-1)^{J-M_J}(JJ M_J - M_J|L0). \]

Classically, \( M_J \) is the projection of \( J \) on an axis at angle \( \alpha \), \( M_J = J \cos \alpha \), and the \( T^M_J \) are \( P_L(\cos \alpha) \) (the \( P_L \) are Legendre polynomials of order \( L \)).

Two distinct \((n+1)\) REMPI techniques for obtaining the alignment of gas phase molecules from photoelectron angular distributions have been proposed by Dubs, Dixit, and McKoy. The first, circular dichroism in angular distributions (CDAD) of photoelectrons, requires that the molecule be excited with \( n \) photons of linearly polarized light and ionized with one photon of left or right circularly polarized light. The CDAD spectrum is the difference between left and right angular spectra:

\[ I_{\text{CDAD}}(\theta) = I_{\text{left}}(\theta) - I_{\text{right}}(\theta), \]

where photoelectron flux is measured as a function of the angle between the polarization of the excitation light and the detector axis. If the excitation and ionization photons propagate along a single line and the photoelectrons are measured in a plane perpendicular to that line, then the CDAD angular spectrum can be expressed as an expansion in associated Legendre polynomials:

\[ I_{\text{CDAD}}(\theta) = \sum_L a_L P_L(\cos \theta) \]

with

\[ a_L = A_L \beta_L, \]

where the \( \beta_L \) contain the dynamics of the ionization, and the \( A_L \) are the multipole moments of the \( n \)-photon excited state.

The other alignment probe scheme differs from CDAD in that the ionization step is done by linearly polarized light, with the polarization vector pointing into the detector, hence the name: polarization-into-detector angular distribution, PINDAD. For counterpropagating excitation and ionization lasers, the PINDAD angular spectrum can be expanded in Legendre polynomials:

\[ I_{\text{PINDAD}}(\theta) = \sum_L a_L P_L(\cos \theta) \]

with

\[ a_L = A_L \beta_L, \]

where the \( \beta_L \) contain the dynamics of the PINDAD ionization, and the \( A_L \) are the same as in Eq. (3). Note that only one angular spectrum is required to obtain \( I_{\text{PINDAD}} \).

A. CDAD data analysis

A method for the determination of ground state alignment by \((n+1)\) CDAD has been presented in Refs. 25 and 27. In the method proposed, the ratio of \( a_2 \) values [Eq. (2)] from two different branches is experimentally determined and used in a simple formula to extract the ground state alignment. The method suffers from the disadvantage that the \( a_2 \) values for two different angular spectra must be determined relative to one another. In practice, this means normalizing each \( a_2 \) value to be the intensity of the left or right photoelectron spectrum at a particular angle, say \( 90^\circ \), and later taking a wavelength spectrum with the detector fixed at that angle in order to determine the relative \( a_2 \) values. While this procedure is certainly feasible, the necessity of a wavelength spectrum is experimentally inconvenient. For this reason, a method of analysis which eliminates this requirement is presented here.

Ideally, the \( a_2 \) values from the CDAD angular spectra would be normalizable by some quantity in the CDAD (left or right) angular spectrum which has the same convenient analytical properties as the CDAD coefficients. The most obvious quantity would be \( a_0 \) proportional to the excited state populations. Unfortunately, unlike the PINDAD case, \( a_0 \) is not analytically obtainable from a CDAD angular spec-
Nevertheless, the area under the left or right angular spectrum is found to be approximately proportional to \( a_0 \); the error is calculated to be on the order of 1%–2% over a wide range of initial state alignments.\(^{38}\) This error is considered to be acceptable for the present purposes. In this regard, it should be pointed out that, while in Ref. 29 (Sec. III C) the intensity of the left or right spectrum at 90°, \( I(90°) \), was shown to be approximately related to \( a_0 \), this approximation was considered only for \( P \) and \( R \) branches. Overall, the error in using \( I(90°) \) rather than the area as an approximation to \( a_0 \) is calculated to be on the order of 10%.

The CDAD \( a_2 \) value normalized by the area under the left or right spectrum, labeled \( \bar{a}_2 \), can now be written as

\[
\bar{a}_2 = \frac{a_2}{\text{Area}} = \frac{A_2 \beta_2}{A_0 \beta_0},
\]

where \( A_0 \) is the excited state population, \( A_2 \) is the excited state quadrupole moment, and \( \beta_2 \) and \( \beta_0 \) contain information about the photoionization dynamics. The excited state alignment \( \tilde{A}_2 \) can be related to the ground state alignment \( \tilde{A}_2 \) by [Eq. (5) of Ref. 25]

\[
A_L = \sum_{k} A_{L,k} \cdot C_{k,L},
\]

\[
A_0 = \tilde{A}_0 C_{00} + \tilde{A}_2 C_{20},
\]

\[
A_2 = \tilde{A}_0 C_{02} + \tilde{A}_2 C_{22},
\]

where \( \tilde{A}_{L,k} \cdot \) is the ground state alignment. Analytical expressions for the \( C_{L,k} \) are given in Table I of Ref. 25.\(^{39}\) The \( J' \) (angular momentum of the excited state) dependence of \( \beta_L \) in Eq. (6) can be factored out [Eq. (19) of Ref. 25]:

\[
\beta_L (J') = X_L (J') \tilde{\beta}_L,
\]

where \( \tilde{\beta}_L \) is explicitly independent of \( J' \) and can be treated as a constant.\(^{35}\) Analytical expressions for \( X_L \) and \( X_2 \) are given in Ref. 25 [Eqs. (21) and (22)].

Using Eqs. (8), (9), and (10), Eq. (6) can be written as

\[
\bar{a}_2 \propto \left[ \frac{A_0 C_{02} + A_2 C_{22}}{A_0 C_{00} + A_2 C_{20}} \right] \frac{X_L \tilde{\beta}_L}{X_0 \tilde{\beta}_0}.
\]

The alignment parameters \( \tilde{A}_0 \) and \( \tilde{A}_2 \) can be related to the parameter \( \delta_0^{(2)} \) commonly extracted from laser-induced fluorescence (LIF) measurements:\(^{28,36}\)

\[
\delta_0^{(2)} = \left[ \frac{(2J + 3)(2J - 1)}{5J(J + 1)} \right]^{1/2} \frac{\tilde{A}_2}{\tilde{A}_0}.
\]

Equation (11) can then be rewritten as

\[
\bar{a}_2 \propto \frac{M_{02} - M_{22} \delta_0^{(2)}}{M_{00} - M_{20} \delta_0^{(2)}} \left( \frac{\tilde{\beta}_2}{\tilde{\beta}_0} \right).
\]

Analytical expressions for the \( M \) values are given in Table I (\( M_{02} \) and \( M_{22} \) are \( M_0 \) and \( M_2 \), respectively, of Ref. 27). (Note that because all \( M \) values appear in ratios, they can all be multiplied by a constant with no consequence.)

For mixed branches, the \( M \) values are simply added. The \( E \) values in the table are the one-photon line strengths (often denoted \( S \)) given by Earls.\(^{41}\) All the information about the photoionization dynamics is contained in the ratio \( \tilde{\beta}_2 / \tilde{\beta}_0 \). This ratio is a constant for all \( J \) and all branches, but is unknown. By determining the ratio of \( \bar{a}_2 \) values for two different branches, however, the photoionization dynamics can be eliminated.\(^{25,27}\) Alternatively, the ratio \( \tilde{\beta}_2 / \tilde{\beta}_0 \) can be determined from independent \((1 + 1)\) CDAD experiments of unaligned NO.\(^{40}\)

The experimentally determined ratio \( R \) of \( \bar{a}_2 \) coefficients for two different branches, \( i \) and \( k \), is given by

\[
R = \frac{\bar{a}_2^{(i)}}{\bar{a}_2^{(k)}} = \left[ \frac{M_{02}^{(i)} - M_{22}^{(i)} \delta_0^{(2)}}{M_{00}^{(i)} - M_{20}^{(i)} \delta_0^{(2)}} \right] \left( \frac{M_{02}^{(k)} - M_{22}^{(k)} \delta_0^{(2)}}{M_{00}^{(k)} - M_{20}^{(k)} \delta_0^{(2)}} \right)^{-1}.
\]

This equation can be inverted to give \( \delta_0^{(2)} \) as a quadratic function of \( R \). (For the range of \( R \) obtained in the present work a plot of \( R \) vs. \( \delta_0^{(2)} \) for \( J = 45.5 \) is given later in Fig. 3.)

The advantages of the above method over the method described in Refs. 25 and 27 are twofold: first, as stated above, a wavelength spectrum to provide the relative magnitudes of the CDAD spectra is no longer necessary; second, problems arising from a difference in populations of the \( A \)-doubled \( F_i \) and \( F_k \) states are eliminated.

The analysis of PINDAD spectra, for which the ratio of \( a_2 \) to \( a_0 \) is obtained analytically from the leading two terms in the Legendre expansion [Eq. (4)], is identical to that just described for CDAD. This method was first suggested in Sec. VII of Ref. 25.

**B. Magic angle PINDAD (MAP)**

Theoretically, the maximum \( L \) in a PINDAD Legendre expansion [Eq. (4)] is limited only by the maximum align-
ment in the photoinitized state. (The maximum L can further be limited by a low value of J′.)

However, in practice, the rapid decrease in the magnitude of \( \beta \) with increasing L causes a strong suppression of the higher order \( a'_n \). If these higher order coefficients, such as \( a'_1, a'_2, \) etc., are ignored and the PINDAD configuration is set to the magic angle of \( \theta = 54.7° \), where \( P_2(\cos \theta) = 0 \), the intensity of the PINDAD signal becomes

\[
I_{\text{MAP}} = I_{\text{PINDAD}}(54.7°) \approx a'_0. \tag{15}
\]

Thus, a wavelength spectrum in the MAP configuration gives peaks whose heights are proportional to the excited state populations only, with no excited state alignment contribution (ignoring \( a'_0, a'_2, \) etc.).

The excited state populations can be written in terms of the ground state population and alignment using Eq. (8),

\[
a'_0 = A_0 \beta_0 = N(J) E [\tilde{A}_0 C_{00} + \tilde{A}_2 C_{20}] \tilde{X}_0 \tilde{B}_0', \tag{16}
\]

where \( N(J) \) is the population of the initial state and \( E \) is the one-photon line strength described earlier. \( N(J) \) is unnecessary in the CDAD equations, described above, because it is eliminated in the ratio \( \bar{a}_2 \). The \( E \) values appear in those equations through \( M \) only because of the possibility of mixed branches. Using Eq. (12) and expressions from Ref. 25, Eq. (15) can be expressed as

\[
P \text{ branch } I_{\text{MAP}} = \frac{EN \tilde{B}_0'}{3(2J + 1)} \left[ 1 - \frac{J + 1}{2J - 1} \vartheta(2^0) \right], \tag{17}
\]

\[
Q \text{ branch } I_{\text{MAP}} = \frac{EN \tilde{B}_0'}{3(2J + 1)} \left[ 1 + \vartheta(2^1) \right], \tag{18}
\]

\[
R \text{ branch } I_{\text{MAP}} = \frac{EN \tilde{B}_0'}{3(2J + 1)} \left[ 1 - \frac{J}{2J + 3} \vartheta(2^2) \right]. \tag{19}
\]

In this case \( \tilde{B}_0' \) is an unknown constant. It should be noted that these equations are identical to those describing polarized fluorescence from an aligned excited state. From an angular momentum point of view, the fluorescence case is identical to the present one of an excited-state population produced by photoabsorption from an aligned ground state. With the ground state alignment \( \vartheta(2^2) \) determined from the CDAD analysis, the MAP wavelength spectrum can be used to determine the ground state populations.

C. Fragment angular distributions

The angular distribution of fragment ions produced by the REMPI technique is a function of the product of probabilities for: (1) dissociation at a given angle \( \theta \) (the direction of the velocity vector \( v \) with respect to the photolysis electric vector \( \epsilon_\rho \)); (2) absorption of a photon by the fragment with transition dipole \( \mu_v \), where the electric vector \( \epsilon_\rho \) polarization is at an angle \( \theta' \) from the velocity vector \( v \); and (3) total ionization cross section. The dynamics of the photolysis will determine the relationship between \( v \) and the fragment angular momentum vector \( J_v \) as well as the relation of these two vectors to the photolysis transition dipole moment \( \mu_v \), which is a function of the electronic structure of the initial and dissociative states of the parent molecule. Derivations of correlations between these vectors have most recently been derived for Doppler broadened spectral line profiles by Dix-}

\[ \text{on}^{19} \text{ and Hall et al.}^{20} \] In this paper we have adapted the approach used by Hall et al., which is somewhat more intuitively transparent, to interpret REMPI ion angular distributions.

In the experimental configuration described above, the photolysis and excitation lasers propagate in the same direction and their polarization vectors are parallel, \( \epsilon_\rho \parallel \epsilon_v \), hence \( \theta' = \theta \). We can therefore introduce a simple coordinate system which is described in detail in the Appendix. The aim is establishing this coordinate system is to obtain an expression for the ion angular distribution based on a correlation between the three vector quantities \( \mu_v, v, J \). This is accomplished by fixing the angles between each of these vectors: \( \theta \) is the angle between \( v \) and \( \mu_v \); \( \chi \) is the angle between \( v \) and \( J_v \); and \( \eta \) is the angle between \( \mu_v \) and \( J_v \). The function describing the angular distribution \( I(\theta, \rho, \chi, \eta) \) is proportional to the probability of exciting the parent molecule to a dissociative state, \( |\mu_v, \epsilon_\rho|^2 \), times the probability of exciting the daughter fragment, \( \left( |\mu_v, \epsilon_\rho|^2 \right)_{\text{a}, \text{b}} \), averaged over all orientations of the parent. (The daughter excitation is averaged over all orientations of the molecule in its rotation plane, perpendicular to \( J_v \).) The angle dependence of the total ionization can be omitted as it is expected to be small.\(^{22,38}\)

The resultant expression for \( I(\theta, \rho, \chi, \eta) \) takes the form of an expansion in Legendre polynomials, i.e.,

\[
I(\theta, \rho, \chi, \eta) \propto b_0[\rho, \chi, \eta] + b_1[\rho, \chi, \eta]P_2(\cos \theta) + b_2[\rho, \chi, \eta]P_4(\cos \theta), \tag{20}
\]

where the \( b_i \) are different for \( P, Q, \) and \( R \) branches. Explicit expressions for the \( b_i \) are given in the Appendix [Eqs. (A12)–(A14)]. Under most experimental conditions \( I(\theta, \rho, \chi, \eta) \) can only be measured to within a proportionality constant so that we define \( B_i = b_i/b_0 \), giving

\[
I(\theta, \rho, \chi, \eta) \propto 1 + b_1[\rho, \chi, \eta]P_2(\cos \theta) + b_2[\rho, \chi, \eta]P_4(\cos \theta). \tag{21}
\]

In general, experimental data are convoluted by the angular resolution of the detector. For data that are described by a Legendre expansion, the fitted coefficients \( \tilde{B}_i \) can be deconvoluted to coefficients for infinite angular resolution \( B_i \) using the relation\(^{43}\)

\[
B_i = \frac{\tilde{B}_i}{P_{l+1}(\cos \delta - 1)} \cdot P_{l-1}(\cos \delta), \tag{22}
\]

where \( \delta \) is the angular width of the detector aperture.

IV. RESULTS AND DISCUSSION

A. General

The absorption spectrum of methyl nitrite in the 227–233 nm range covered by this work consists of a very broad featureless band \( (S_\lambda) \) centered at 210 nm. This band has been assigned to a \( \pi^* \rightarrow \pi \) transition involving an overall charge transfer from the methoxy group to the \(-\text{NO moiety.}^{44}\) The diffuse nature of this band is consistent with a featureless band \( (S_2) \) centered at \( 381 \text{ nm.} \)

\[
\text{CH}_3\text{ONO} + hv \rightarrow \text{CH}_3\text{ONOO}^*(S_2) \rightarrow \text{CH}_3\text{O}^-(X) + \text{NO}(X^2\Pi, \nu, J). \tag{23}
\]
The threshold energy for this dissociation is 1.8 eV, so that substantial excess energy (-3.8 eV) is available for partitioning among the translational and internal degrees of freedom of the two photofragments. At wavelengths longer than 210 nm only the ground electronic states of CH$_3$O and NO are accessible while at shorter wavelengths CH$_3$O can be produced in its $^2A_1$ electronically excited state. The repulsive nature of the $S_2$ state has recently been confirmed by Huber and co-workers who measured the CH$_3$O- and NO translational energies and angular distributions by electron-impact photofragment spectroscopy at 248 nm. This group found that 53% ± 3% of the excess energy appears as translational energy of the fragments, in good agreement with a value of 49% expected for an impulsive dissociation mechanism involving an unbound upper state. Methyl nitrite in the $S_0$ state exists as either the cis or trans planar (considering only the CONO) isomer; at 300 K the cis form is preferentially populated over the trans by a factor of 1.75. On the basis of the Franck-Condon principle and the repulsive nature of the $S_2$ potential energy surface one can readily assume that the $S_2$ state will retain the $S_0$ geometry upon excitation. Photofragment angular distributions characterize the $S_2$ absorption as a parallel transition with the transition dipole moment $\mu_p$ lying in the molecular plane. The high value of the photoion asymmetry parameter ($\beta = 1.4 \pm 0.1$) is also consistent with a prompt dissociation mechanism in which fragmentation is on the same time scale as parent rotation.

Additional dynamical information including internal state distributions, alignment, and other vector correlations can be derived from laser probes of the photofragments. The nascent rotational and vibrational states of NO fragment can be probed by excitation with linearly polarized light to the $^2\Sigma$ state:

$$\text{NO}(X^2\Pi, v, J) + h\nu(-225 \text{ nm}) \rightarrow \text{NO}(^2\Sigma, v', J').$$

(24)

The population and alignment of the $^2\Sigma$, $v', J'$ state are probed by ionizing the NO with circularly or linearly polarized light:

$$\text{NO}(^2\Sigma, v', J') + h\nu(266 \text{ nm}) \rightarrow \text{NO}^+ + e^-.$$  

(25)

Since the one-photon excitation process $^2\Sigma \rightarrow ^2\Pi$ is easily characterized, populations, alignments, and vector correlations can be obtained for the $X^2\Pi, v, J$ state of the NO fragment from the photoelectron and photoion signals.

For NO in its $^2\Pi$ state one cannot speak of one ground state but rather of four. The two spin states $F_1 (^2\Pi_{1/2})$ and $F_2 (^2\Pi_{3/2})$ arise from two possible spin-orbit couplings of the total nonspin angular momentum $K$ and the spin angular momentum $S$, yielding the total angular momentum $J = K + S$, in which $J = K + 1/2$ for $F_1$ and $J = K - 1/2$ for $F_2$. Each of these spin states is further split by weak coupling (A doublet) of the electronic angular momentum $L$ with the rotation of the nuclei. This coupling is weak in Hund’s cases (a) and (b), however each of the $\Lambda$ states ($\Lambda = \pm 1$ for an $\Pi$ state) have different parities. In the case of NO, the $\Lambda$ doublets arise from two orientations of the unpaired $\pi_r$ electron lobe which lies perpendicular to the molecular axis of the NO and is either (1) parallel to $J$ or (2) perpendicular to $J$. The symbols $\Pi_{+}$ and $\Pi_{-}$ designate cases (1) and (2), respectively. The $\Pi_{+}$ states are probed with the $Q_{11} + P_{11}$ and $Q_{22} + R_{22}$ branches (and also $R_{11}$ and $P_{12}$); and $\Pi_{-}$ states are probed with the $P_{11}$ and $P_{22} + Q_{12}$ branches (and also $R_{11} + Q_{21}$, and $R_{22}$).

### B. Magic angle PINNAD spectrum

The magic angle PINNAD (MAP) configuration provides a relatively simple means for obtaining ground state rotational populations, as is evident from Eqs. (17)-(19). Figure 1 shows a MAP spectrum of NO produced from the dissociation of methyl nitrite. Two distinct features are apparent: (1) at longer wavelengths the bandhead region shows NO at relatively low $J$; (2) at shorter wavelengths very high-$J$ photofragments are observed. The low-$J$ region is attributed to NO contaminant in the sample. Indications that this region is indeed due to free NO and not an alternate dissociation path come from the photoion time-of-flight spectra; the long wavelength region shows a very sharp and narrow peak corresponding to a low velocity NO; while the short wavelength region shows two distinct peaks (see end of Sec. II) corresponding to NO with an average energy of $\pm 1$ eV. It is extremely improbable that NO with low $J$ is a product of photodissociation; very low translational and low rotational energy products are inconsistent with high excess energy (~3.8 eV) above dissociation, particularly for the nonlinear RO-NO geometry. (If this were the case then all of the photolysis energy would be channeled into internal degrees of freedom of the -OCH$_3$ radical; conservation of angular momentum would then dictate that these be vibrational modes.)

The lower panel of Fig. 1 shows the high $J$ region in detail with assignments for four of the strongest NO branches: $P_{11}$, $Q_{11} + P_{21}$, $Q_{22} + R_{12}$, and $P_{22} + Q_{12}$. (The $R_{11} + Q_{21}$ and $R_{22}$ branches are expected to peak at similar $J$, which would place the strong lines of these branches at shorter wavelengths and outside the range of the figure.) The $R_{21}$ and $P_{12}$ branch lines are present in our spectrum, but as they are weak we do not report their assignment. The assignment is based on molecular constants for the $^2\Pi$ and $^2\Sigma$ states listed in Huber and Herzberg and expressions for the energies of these states given in Herzberg. Relative populations of the $^2\Pi$, $v = 0$ rotational states can be extracted from the spectral line intensities (peak heights, see Sec. II) by using Eqs. (17)-(19). The branch and $J$ dependent line strengths $E$ are easily calculated. The only unknown in these equations is the alignment $a_0^{(2)}$, which is obtained from the CDAD measurements (the other unknown, $\beta_0$, is unimportant for relative population measurements). Once the alignment is known then populations $N(J)$ can be reported for each of the branches. An examination of Fig. 1 reveals that the MAP signal for the $Q$ branches is much lower than for $P$ branches. In the case that $a_0^{(2)} = 0$ and $N(J)$ are equal for all initial $\Lambda$-doublet states, the line strengths $E$ dictate that $I_{\text{MAP}}$ should be higher for a $Q_{11} + P_{12}$ branch (probing $F_1 \Pi_{1/2}$) than for a $P_{12}$ branch (probing $F_1 \Pi_{3/2}$) by a factor of $\approx 2$. (The $P_{12}$ component makes a small contribution to the $Q_{11} + P_{12}$ branch, being about a factor of 10 lower than the $Q_{11}$ component.) As is
shown in the next section, the decrease in the Q branch intensity can be attributed to a negative $\alpha_2^{(2)}$ and/or to a lower population for initial A-doublet states probed by that branch.

C. Alignment from CDAD

Representative CDAD spectra are shown in Fig. 2 and are summarized in Table II in terms of the $\alpha_j$ coefficients of Eq. (6). The most striking feature of the photolysis CDAD spectra is the apparent lack of CDAD signal for the Q branches ($\bar{\alpha}_2$~0). This result is in contrast to the CDAD spectrum for free, unaligned NO (dashed line, $\bar{\alpha}_2$~ + 0.069). On the other hand, photolysis CDAD spectra for the P branches are enhanced relative for unaligned NO. (The free NO spectra are from a previous study 29 for different J, but are expected 38 to resemble closely those branches of interest here at $J = 45.5$.) As discussed below, these observations are a direct signature of a high negative value for $\alpha_2^{(2)}$. The experimentally derived ratio $R = \frac{\bar{\alpha}_2^{(Q_1 + P_2)}}{\bar{\alpha}_2^{(P_2)}}$ [Eq. (14)] for a range of J's in Table II results in a value of $\alpha_2^{(2)} = - 0.45 \pm 0.04$ averaged over J and both the $P_1$ and $P_2$ states. The relationship between $R$ and $\alpha_2^{(2)}$ at $J = 45.5$ is shown graphically in Fig. 3. Because the values of $\bar{\alpha}_2^{(Q_1 + P_2)}$ are very small, and therefore difficult to determine accurately, the $R$ values have a corresponding uncertainty associated with them. However, as is evident from Fig. 3, the value of $\alpha_2^{(2)}$ is fairly insensitive to small changes in $R$ about $R = 0$.

For an initial state with an alignment characterized by $\alpha_2^{(2)} \sim - 0.4$, low $|M_J|$ substates have a greater population relative to high $|M_J|$ states. Upon photoabsorption, the effect of a Q transition is to "wash out" this $M_J$ anisotropy in the excited state. Specifically, the initial state alignment, with low $|M_J|$ preferentially populated, is reduced in the excited state by the relative Q branch transition probabilities which preferentially excite high $|M_J|$ levels ("parallel" transitions, $J||\mu_s$). This trend is confirmed quantitatively by comparing the $A_0/A_0$ ratio for an excited state populated via a Q branch transition from an unaligned initial state ($\alpha_2^{(2)} = 0.0$), $A_0/A_0 = + 0.89$, to that for an aligned initial state with $\alpha_2^{(2)} = - 0.4$, $A_0/A_0 = + 0.32$. This drop in $A_0/A_0$ is accompanied by an increase in the hexadecapole moment, $A_0/A_0$, which changes from 0.0 to 0.57 for initial state alignment of $\alpha_2^{(2)} = 0.0$ and $\alpha_2^{(2)} = - 0.4$, respectively.

FIG. 1. Magic angle PINAD spectrum of NO $(v = 0)$ from the photodissociation of CH$_3$ONO. The left (longer wavelength) region corresponds to free NO. The lower panel is an expansion of the region corresponding to high J.
Table II. CDAD fitting and alignment parameters.

<table>
<thead>
<tr>
<th>Branch</th>
<th>$J^*$</th>
<th>$\tilde{a}_2$</th>
<th>$\alpha_0^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{11}$</td>
<td>35.5–36.5</td>
<td>-0.085</td>
<td>-0.45 ± 0.05</td>
</tr>
<tr>
<td>$Q_{11} + P_{21}$</td>
<td>44.5–46.5</td>
<td>-0.074</td>
<td>-0.46 ± 0.04</td>
</tr>
<tr>
<td>$P_{21}$</td>
<td>45.5–46.5</td>
<td>0.015</td>
<td>0.008</td>
</tr>
</tbody>
</table>

The hexadecapole contribution is not reflected in the CDAD spectrum due to the small value of $b_{14}$. However, this does not mean the alignment is characterized by quadrupole moments only (for a fragment-velocity-averaged ensemble).

For a $P$ or $R$ branch transition where low $M_f$ substates are preferentially excited ("perpendicular transition" $J\mu\nu$), the initial state alignment of $\alpha_0^{(2)} \sim -0.4$ enhances the excited state alignment relative to the case for excitation from an unaligned state. This increase is reflected in the $P_{11}$ (45.5) CDAD spectra of Fig. 2. The enhancement of alignment in the $P$ branch further contributes of the lack of $Q$ branch CDAD intensity (Fig. 2), because the mixed branch $Q_{11} + P_{21}$ has both a depressed $Q$ alignment and an enhanced $P$ alignment which tend to cancel. The strong negative alignment of the NO photofragment is consistent with the MAP spectrum (Fig. 1) which shows a strong enhancement of $P$ branch lines relative to $Q$ branch lines as is predicted by Eqs. (17)–(19).

The experimental result $\alpha_0^{(2)} = -0.45 ± 0.04$ should be compared to its theoretical limit. For fragment alignment created by one-photon dissociation, only the $L = 0$ and 2 terms of Eq. (1) are applicable, and this equation can be written explicitly as

$$N_{M_f} = \frac{1}{2J+1} \left[ 1 + \frac{5[3M_f^2 - J(J+1)]}{(2J+3)(2J-1)} \right] \alpha_0^{(2)}.$$  

This equation gives the relative initial $M_f$ state populations for a given initial state alignment. The fact that the value of $N_{M_f}$ represents a population, and therefore cannot be less than zero, imposes the following constraint on $\alpha_0^{(2)}$:

$$\alpha_0^{(2)} > \frac{-(2J+3)}{5J},$$

where this lower limit is obtained by requiring that $N_{M_f}$ be nonnegative. For $J = 35.5$ Eq. (27) provides the limit $\alpha_0^{(2)} > 0.417$ while for $J = 45.5$, $\alpha_0^{(2)} > -0.413$.

The experimental result $\alpha_0^{(2)} = -0.45 ± 0.04$ is consistent with these limits within the given experimental error. Note that for high $J$, Eq. (27) approaches the well known classical limit $\alpha_0^{(2)} > -0.4$.

While the $J$-averaged experimental $\alpha_0^{(2)}$ is consistent with theoretical limits discussed above, the results appear to be systematically lower (more negative) than these limits.

FIG. 2. CDAD angular distributions of NO ($\nu = 0$) from the photodissociation of CH$_3$ONO. The + are experimental data. The solid curves are best fits to the data using Eq. (2), with $L = 2$ and 4. The dashed curves are for free (unaligned, $\alpha_0^{(2)} = 0$) NO (see note in Sec. IV C of the text).

The experimental result $\alpha_0^{(2)} = -0.45 ± 0.04$ should be compared to its theoretical limit. For fragment alignment created by one-photon dissociation, only the $L = 0$ and 2 terms of Eq. (1) are applicable, and this equation can be written explicitly as

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This equation gives the relative initial $M_f$ state populations for a given initial state alignment. The fact that the value of $N_{M_f}$ represents a population, and therefore cannot be less than zero, imposes the following constraint on $\alpha_0^{(2)}$:

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While the $J$-averaged experimental $\alpha_0^{(2)}$ is consistent with theoretical limits discussed above, the results appear to be systematically lower (more negative) than these limits.
Two factors can be suggested to account for this result: (1) saturation in the excitation of the NO fragment could distort the $M_J$ distribution in the $A$ state; (2) incomplete overlap of the laser linewidth with the Doppler-broadened NO absorption line could result in preferential sampling of certain fragment velocities. Although we measured CDAD signals at a range of laser energy densities, and found no detectable change in the fitted $a_P$ parameters, we cannot completely rule out small saturation effects because the dynamic range of this experiment is too small to perform a complete power dependence study. Jacobs, Madix, and Zare have demonstrated that a one-color $1 + 1$ REMPI spectrum of NO cannot be completely free of saturation; at energy densities below 0.5 mJ/cm$^2$ saturation does not appear to be a significant complication, while at 5 mJ/cm$^2$ it may be a problem. Under the operating conditions outlined in the experimental section an energy density near 5 mJ/cm$^2$ is achieved. This may present a difficulty for the branches with low CDAD signal, $Q_{11} + P_{21}$ and $Q_{22} + R_{12}$, where even a small degree of saturation could reduce the already small $a_P^2$.

The second problem was found to be significant in laser fluorescence studies of photodissociation products, where alignment was strongly influenced by the laser linewidth. In our experiments the laser linewidth is $\approx 1.3$ cm$^{-1}$ (full width at half-maximum), which is broader than the Doppler width of 0.74 cm$^{-1}$ (full width at base line) for 1 eV NO fragments. Although the Gaussian laser line completely envelopes the Doppler profile (which has a rather sharp rise and fall at the base line), to some extent it preferentially samples the center of the profile where laser intensity is greatest. The Doppler profile center corresponds to fragment velocities $v$ which are parallel to the laser polarization ($e_p$) as a result of the highly peaked photofragment angular distribution along $e_p$. Since $J$ is essentially perpendicular to $v$ (see Sec. 4V E), fragments at the Doppler profile center will also have $J$ perpendicular to $e_p$ which corresponds to $M_J$ distributions peaked near $|M_J| = 0$. Preferential excitation of these fragments would result in an apparently more negative $a_P^2$.

In light of the above discussion, we conclude that the NO fragments from photodissociated methyl nitrite are at the maximum (most negative $a_P^2$) alignment for both the $F_1$ and $F_2$ initial states. This result indicates that low $M_J$ states are preferentially populated in the photoproducts, such that the angular momentum vector $J$ is perpendicular to the electric vector $e_p$ (the axis of quantization), and therefore to the photoysis transition dipole moment of the parent $\mu_p$ during photofragmentation ($\eta = 90^\circ$).

**D. Rotational state populations**

The state distributions $N(J)$ for the $F_1\Pi_A$, $F_1\Pi_{A'}$, $F_2\Pi_A$, and $F_2\Pi_{A'}$ levels of the $X$ state of NO are obtained from the aligned correction MAP intensities for the $P_{11}$, $Q_{11} + P_{21}$, $P_{22} + Q_{12}$ and $Q_{22} + R_{12}$ branches, respectively, and are shown in Fig. 4. The overall population distribution is well characterized by a Gaussian distribution (also shown in Fig. 4) with a peak value of $J_p = 51 \pm 2$ and width at half-maximum of $J_{FWHM} = 12 \pm 2$. These fitted parameters can only be viewed as representative since the experimental data are limited to rotational levels with $J<55.5$. Gaussian-like rotational state distribution have also been found for NO photofragments produced via the $S_1$ state of CH$_3$ONO$^6$,$^{10,12}$ and other precursor molecules such as (CH$_3$)$_2$N-NO$_7$, CINO$^{46}$, and (CH$_3$)$_2$CONO$^{17}$ Quantal and classical trajectory calculations by Schinke$^{51,52}$ have shown that inverted (highly non-Boltzmann) rotational distributions are a natural consequence of rotational–translational coupling in the direct dissociation of pseudodiotropic molecules. Furthermore, Schinke found that rotational distributions are governed by the "rotational reflection principle" in which the distribution of rotational angular momentum of the diatomic fragment reflects the distribution of initial orientation angles (representative of the nonlinearity) of the parent molecule. According to the rotational reflection principle, the high degree of population inversion observed in Fig. 4 results from a highly anisotropic $S_1$ potential energy surface above the bent ground state ($S_0$) equilibrium geometry. Calculations of this type could provide additional information on the extent of the rotational–translational coupling in the repulsive $S_1$ state and the distributions of O–N–O bending and torsion angles in the initial $S_0$ state.

Assuming that the Gaussian fit in Fig. 4 correctly describes the NO ($X, \nu = 0$) rotational distribution, we obtain an average rotational energy of $(E_{rot}) = 4600 \pm 200$ cm$^{-1}$. This value brackets the result obtained from impulsive model calculations ($E_{rot} = 4600$ cm$^{-1}$) of Keller et al.$^{4,5}$ using ·CH$_3$ and NO photofragment translational energies measured at 248 nm ($S_1$ dissociation). In the impulsive model, rotational excitation results from the torque exerted on the molecular fragment by the motions of the recoiling atoms along the dissociation coordinate. Scaling the impulse model calculations for the increase in total available energy, we estimate $(E_{rot}) = 5340$ cm$^{-1}$ at a dissociation wavelength of 225 nm which corresponds to the center wavelength of the MAP spectrum (Fig. 1). Given the approximation nature of such calculations and the limitations of the fit in Fig. 4, the agreement with experiment is quite satisfactory and suggests that the mechanism for producing rotationally
excited NO via S₂ dissociation is well described by the impulsive model. The relative preference for dissociation into the four electronic state channels \( F_1(\Pi_{\text{A}^+}), F_1(\Pi_{\text{A}^-}), F_2(\Pi_{\text{A}^+}), F_2(\Pi_{\text{A}^-}) \) of NO \((X^2\Sigma^+)^\mathcal{N} \) was obtained by averaging the rotational population data (over \( J \)) in Fig. 4 for the appropriate rotational excitation branches. The results can be summarized as follows:

\[
\frac{N(F_1)}{N(F_2)} = 1.4 \pm 0.1 (F_1),
\]
\[
\frac{N(F_1)}{N(F_2)} = 0.9 \pm 0.1 (F_2),
\]
\[
\frac{N(F_1)}{N(F_2)} = 1.3 \pm 0.1 (\Pi_{\text{A}^+}),
\]
\[
\frac{N(F_1)}{N(F_2)} = 0.85 \pm 0.1 (\Pi_{\text{A}^-}).
\]

The \( F_1(\Pi_{\text{A}^+})/\Pi_{\text{A}^-} \) channel is favored above all others and the \( F_1(\Pi_{\text{A}^-}) \) spin–orbit state shows preferential alignment of the lone \( p \) \( r \) orbital in the plane of rotation \( N(\Pi_{\text{A}^+}) > N(\Pi_{\text{A}^-}) \). This “electronic alignment” of the \( F_1 \) levels can be rationalized given the \( \Sigma_+ \rightarrow \Sigma_- \) dissociation dynamics as inferred so far. Specifically, the \( \Sigma_- \) state is known to be of \( A' \) symmetry \( (C_2v \) symmetry group \) which requires the \( \Sigma_- \) electronic wave function to be symmetric with respect to reflection in the \( C=O-N=O \) molecular plane. Consequently, the \( p r \) orbitals of the NO molecule which contribute to the \( \pi^* \) molecular orbital \( (a') \) must also lie in that plane. Since photodissociation via the \( \Sigma_- \) state results in NO fragments preferentially rotating in the molecular plane \( (\theta = 0) \), an enhanced population in the \( \Pi_{\text{A}^-} \) component of the \( p r \) orbital is expected. Similar qualitative arguments have been used to rationalize the \( \Lambda \)-doublet populations resulting from the \( \Sigma_+ \rightarrow \Sigma_- \) dissociation of other alkyl nitrites.\(^{3,6,11,16,17}\) For the \( F_2(\Pi_{\text{A}^-})/\Pi_{\text{A}^+} \) states the \( \Lambda \)-doublets are populated nearly equally. By contrast, Schwartz-Lavi and Rosenwachs\(^{17}\) obtained quite different \( N(\Pi_{\text{A}^+})/N(\Pi_{\text{A}^-}) \) ratios in a very recent study of the \( \Sigma_- \) dissociation of the closely related system, \( t \)-butyl nitrite. They find that the \( \Pi_{\text{A}^-} \) levels are strongly preferred for \( 49.5<J<60.5 \) with an average \( N(\Pi_{\text{A}^+})/N(\Pi_{\text{A}^-}) \) of 1.2.7. In order for the \( \Sigma_- \) state to be of overall \( A' \) symmetry, they rationalized that the unobserved \( OC(CH_3)_3 \) fragment must also have \( A^* \) symmetry. Although \( \Sigma_- \) photodissociation for both parent molecules leads to NO photofragments with similar rotational alignments and rotational state distributions \( (\Delta \theta = 0) \), the disparity in the \( \Lambda \)-doublet populations reflects subtle differences in their respective dissociation mechanisms.

The results for the rotationally averaged \( N(F_1)/N(F_2) \) ratios given above show a spin–orbit preference for the \( \Pi_{\text{A}^+} \) levels whereas an approximately statistical ratio is found for the \( \Pi_{\text{A}^-} \) components. The data of Schwartz-Lavi and Rosenwachs\(^{17}\) for \( t \)-butyl nitrite also show a small preference for the \( F_1 \) state of NO following \( \Sigma_+ \rightarrow \Sigma_- \) photodissociation. In general, spin alignment is not expected in the direct dissociation of repulsive singlet states unless curve crossing occurs to higher spin states in specific exit channels.\(^{3,5}\) Specific mechanisms have been invoked to account for such spin alignment in \( CN(X^2\Sigma^+) \) and \( OH (X^2\Pi) \) from photodissociation of ICN\(^{36}\) and HONO\(^{3}\) respectively, however, such mechanisms are not readily generalized to the present study. In any case, the \( F_1 \) and \( F_2 \) states represent distinct dissociation channels and their relative yields should be a sensitive probe of additional energy and angular momentum transfers not considered in simple impulsive dissociation models.

### E. Photoion angular distributions

Figure 5 shows the time-of-flight distribution of NO photoions at a representative range of wavelengths, at \( \theta = 0^\circ \). Given the geometry of the drift and accelerating regions, the TOF difference between the fast (forward) and slow (backward) NO\(^+\) photoions at \( 0^\circ \) can be used to obtain an estimate of the NO fragment translational energy imparted by dissociation. A translational energy of \( \approx 1 \) eV is obtained from this analysis which is very close to that measured\(^{3,5}\) for NO fragments produced at 248 nm when scaled to reflect the increase in excess energy at 223.5 nm \((\langle E_\text{r} \rangle)_{2235} \approx 1.17 \) \((\langle E_\text{r} \rangle)_{248} = 8140 \text{ cm}^{-1} = 1.01 \) eV. In principle, it is also possible to use photoion TOF data such as that shown in Fig. 5 to extract the translational energy distribution for each \( J \) and thereby provide a more detailed energy partitioning of the dissociation process, particularly for the unobserved \( \cdot OC(CH_3)_3 \) fragment. Although desirable, such an investigation is beyond the scope of the present work.

Photoion angular distributions for the \( P_{11} \) and \( Q_{11} + P_{21} \) branches with \( J = 46.5 \) are presented in Fig. 6. A fit of the experimental data to fourth order Legendre polynomials \([\text{Eq. } (20)]\) is shown as the solid line. Since the velocity of the fragment NO is so much greater than that for the parent CH\(_3\)ONO, the lab to center-of-mass transformation angle \( \Theta \) is small \((\theta = \Theta = \Theta - \Theta) \), where \( \Theta = \sin^{-1} \), \( v_{\text{cm}}/v_{\text{NO}} \), \( v_{\text{cm}} \) is the velocity of the center-of-mass system in the center-of-mass frame, and \( v_{\text{NO}} \) is the velocity of the NO fragment in the center-of-mass frame\(^{39}\) and therefore the lab and center-of-mass angles are virtually the same. The fitting coefficients \( B_i \) and \( \tilde{B}_i \) are corrected (deconvoluted) for the detector collection angle using Eq. (22) and then used to extract the angles \( \rho, \psi, \chi, \) and \( \eta \). The results for the four substates of NO at \( J = 46.5 \) are summarized in Table III. Since the CDAD results indicate a maximum alignment with

![FIG. 5. REMPI photoion time-of-flight spectrum of NO(ν = 0) photoproduct as a function of wavelength. The polarization of the dissociation–excitation laser is along the detector axis (θ = 0).](http://jcp.aip.org/jcp/copyright.jsp)
characterizing the solid curves are given in Table III.

FIG. 6. Normalized REMPI photoion angular distributions of photofragment branches dependent (see Appendix); consequently, very similar angular correlations ($\rho$, $\chi$, $\eta$) can result in quite different $B_i$.

The dashed curves in Fig. 6 are for the case of $\rho = 27^\circ$, $\eta = 90^\circ$, and $\chi = 90^\circ$. The value of $\rho = 27^\circ$ was obtained by Keller et al.45 from a study of the total (unresolved internal states) angular distribution for $S_2$ photolysis at 248 nm. This set of correlation angles corresponds to a dissociation mechanism which is constrained to a plane containing the $\tilde{O}$–$\tilde{N}$–$\tilde{O}$ group and $\mu_p$. The fact that these angles reproduce the basic features of the experimental photoion angular distributions (Fig. 6) attests to the overall correctness of a planar dissociation process.

The gross features of the curves in Fig. 6 can be anticipated from the CDAD alignment result, $\eta = 90^\circ$, which indicates that $J\parallel e_p$, and from the essentially planar geometry of the dissociation complex. For a fast dissociation of planar excited CH$_3$ONO* it is expected that $J$ be approximately perpendicular to $v$. If we assume that $\rho (v\parallel e_p)$ is small, the majority of the NO fragments appear along the direction of the electric vector $e_p$, with $J$ perpendicular to $e_p$ ($\parallel \| e_p$).

Since $P$ and $R$ branches are perpendicular transitions they will be preferentially excited at $\theta = 0^\circ$ (and $180^\circ$) since $J\parallel e_p$. Since the NO flux peaks at these angles high REMPI ion signals can be accounted for. In contrast, $Q$ branches, which are parallel transitions, should be preferentially excited when $\theta = 90^\circ$ ($J$ is now parallel to $e_p$), however the fragment flux is a minimum at this angle. Therefore $Q$ branch transitions will have minima at $\theta = 0^\circ$ and $180^\circ$ due to low $Q$ branch excitation probability, and at $\theta = 90^\circ$ due to low NO flux. These expectations are qualitatively borne out in the results shown in Fig. 6 and the $F_1\Pi_A$, $F_2\Pi_A$, and $F_2\Pi_A$ results listed in Table III, but not for the $F_2\Pi_A$ state. The $J-\nu$ correlation for the $F_2\Pi_A$ state indicates a significant deviation from planarity, $\chi = 62^\circ$, in the dissociation complex. At this value of $\chi$ the $F_2\Pi_A$ angular distribution curve resembles that for $F_1\Pi_A$, rather than the $F_1\Pi_A$. The sensitivity of the $F_2\Pi_A$ to $\chi$ is quite dramatic in the range $65^\circ < \chi < 75^\circ$, where the $B_2$ coefficient changes from $0.78$ ($\chi = 75^\circ$) to $+0.20$ ($\chi = 65^\circ$) with $\rho = 20^\circ$ and $\eta = 85^\circ$ ($B_2 = 0.86$ for $\chi = 75^\circ$, while $B_2 = 1.17$ for $\chi = 65^\circ$). The sensitivity of the $B_2$ and $B_4$ coefficients varies with each angle, $\chi$, $\rho$ and $\eta$, and their range of values; in general, a $5^\circ$ change in one of the angles results in a $5\%–10\%$ change in the coefficients.

The vector correlations summarized in Table III are very distinct for each of the spin–orbit, $\Lambda$–doubled state. According to the rotational reflection principle,$^1$ a specific geometry of the ground state parent molecule results in a specific vibrational–rotational state as well as a specific geometrical relation of the fragments with respect to the parent molecular frame. A broader interpretation of the rotation reflection principle may imply that each of the four states, $F_1\Pi_A$, $F_1\Pi_A$, $F_1\Pi_A$, and $F_2\Pi_A$, originate from different geometries of ground state methyl nitrite. Since the equilibrium (most probable) geometry of the CH$_3$ONO is planar, the predominant fragment orientations should reflect this geometry. Photofragmentation from a strictly planar geometry of the CH$_3$ONO will result in $\chi = 90^\circ$. To some extent this is the case, because for the $F_1\Pi_A$ state, which is the most fa-

<table>
<thead>
<tr>
<th>State</th>
<th>$B_2$</th>
<th>$B_4$</th>
<th>$\rho$</th>
<th>$\chi$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1\Pi_A$</td>
<td>1.78</td>
<td>0.30</td>
<td>24(2)$^*$</td>
<td>83(2)$^*$</td>
<td>90(2)$^*$</td>
</tr>
<tr>
<td>$F_2\Pi_A$</td>
<td>0.86</td>
<td>-0.95</td>
<td>23(2)$^*$</td>
<td>79(2)$^*$</td>
<td>90(2)$^*$</td>
</tr>
<tr>
<td>$F_1\Pi_A$</td>
<td>1.75</td>
<td>0.04</td>
<td>20(2)$^*$</td>
<td>70(3)$^*$</td>
<td>87(3)$^*$</td>
</tr>
<tr>
<td>$F_1\Pi_A$</td>
<td>1.30</td>
<td>0.44</td>
<td>22(2)$^*$</td>
<td>62(3)$^*$</td>
<td>83(3)$^*$</td>
</tr>
</tbody>
</table>

$^*$NO, $\nu = 0, J = 46.5$.

1The $F_1\Pi_A$ state is probed by $P_{11}$ branch, the $F_1\Pi_A$ by the $Q_{11} + P_{22}$, the $F_1\Pi_A$ by the $P_{21}$, and the $F_1\Pi_A$ by the $Q_{22} + P_{12}$.

2The $B_2$ and $B_4$ parameters are fitted to the data manually by varying the angles such that best agreement is attained between the calculated and experimentally extracted $B_2$ and $B_4$ coefficients. (Figure 7 provides a useful visual representation of the three vectors and the angles between them, on the molecular frame of the methyl nitrite molecule in the process of dissociation.) It should be noted that the $B_2$ and $B_4$ coefficients are strongly branch dependent (see Appendix); consequently, very similar vector correlations ($\rho$, $\chi$, $\eta$) can result in quite different $B_i$.

vored dissociation channel, χ is closer to 90° than for the 
F,Πς state. Since nonplanar geometries are less probable,
one could account for the lower yield of NO in the F,Πς state.
In addition, smaller χ angles could result from a “twist” induced by the S2 potential energy surface in specific channels.
Clearly, in order to distinguish the effects of par-
tent geometry and features of the potential energy surface a
calculation of the S2 surface is necessary as well as an eval-
uation of the dynamics on that surface.

The values of ρ extracted from the fits of the data in
Table III are not necessarily inconsistent with that obtained
by Keller et al.,4,5 (ρ = 27°), since their results correspond to
ρ averaged over all states of the NO fragment. For the F, 
(2Π1/2) levels, the Πς and Πς components exhibit very
different ρ angles (μ,λ,υ) which would appear to be corre-
lated to the distinct orientations of the NO one-electron pr orbital relative
to the dissociation plane. The distinction is reduced for the F, (2Π1/2) final states where nonplanar
conformations of CH3ONO (implied by χ <70°) are seem-
ingly more important.

The photoion angular distributions for the F, states are
best fitted with η = 87° (Πς,;) and 83° (Πς,;), which deviate
from the CDAD result of a maximum alignment, η = 90°. These are not significant deviations in light of the error range
in the CDAD and photoion data. It should be pointed out
that this method of analysis of REMPI photoion angular
distributions does not include weighted distributions of
angles ρ, χ, and η; each angle is assumed to have a fixed value.
Therefore, these reported angles represent most probable
values rather than rigid quantities. Nonetheless, our data
provide an example of a method for quantitatively obtaining
angular correlations in terms of angles between relevant
dynamical vectors. These correlations can be employed to infer
detailed characteristics of the dissociation mechanism, such
as the geometry of the parent molecule and the shape of the
dissociative surface.

V. SUMMARY

A combination of angle-resolved photoelectron and
photoion REMPI techniques have been used to probe
NO(X-3Π,υ = 0) photofragments produced by dissociation of
CH3ONO via the S2 state. Photoelectron measurements in
the CDAD and PINDAD configurations yielded initial state
alignments (J,μp) for the first time and provided rotational
and electronic state distributions. A semiclassical analysis
scheme has been presented for extracting vector correlations between μp, v, and J from photoion angular
distributions.

The qualitative features of the S2 dissociation process as
d derived from earlier investigations4,5,32,4 and from this work
are shown pictorially in Fig. 7. Photoexcitation to the repul-
sive S2 state results in dissociation in which electronic energy
is channeled into an “impulse” along the RO-NO bond re-
sulting in a rotation and translation of the fragments as the
bent parent molecule breaks up. Recoil of the fragments
along the dissociation coordinate creates a torque which is
responsible for the NO fragment rotation with J nearly per-
pendicular to the molecular plane of the parent. The high
translational (⟨Et⟩≈8100 cm−1) and high rotational

FIG. 7. Diagram of photodissociating methyl nitrite. The S2 (4A')→S1(4A')
transition dipole moment μp, the velocity v, and the angular momentum J
of the NO fragment are superimposed over the molecular frame, along with
the appropriate angles between these vectors.

(J = 51 and ⟨Erot⟩≈4600 cm−1) energies of the NO photofragment imply a very fast dissociation with minimal ran-
domization of internal degrees of freedom in the photexcited
CH3ONO. These energies are in substantial agreement
with that expected from impulsive model calculations4,5 which are based on a dissociation mechanism essentially identical to that described above.

The highly non-Boltzmann distribution of rotational
states is consistent with the rotation reflection principle for
dissociation involving a range of −O−N−O bending and
torsional motions in the initial state (S2) and a strongly repul-
sive upper state. The principle indicates that specific ro-
tational and vibrational states of photoproducts originate
from specific geometries of the ground state parent. The
spin–orbit, A-douplet states have the same distribution of rotational states, but not the same relative populations. The favored dissociation exit channel is via the F,Πς state, wherein the single electron pr orbital is in the NO plane of rotation. The F,Πς state is preferentially populated by a factor of ~1.4 over the other three channels.

The alignment of the NO fragment, as obtained from the
CDAD data, is at the theoretical limit for both the F, and F, states; the experimental value for the alignment parameter is

\[ \langle J, \mu_p \rangle = -0.45 \pm 0.04 \]

These results indicate that the angular momentum vector J is perpendicular to the photolysis transition dipole moment μp; i.e., the J−μ correlation angle η is 90°.

Additional vector correlations, between v and μp, and
between J and v, substantiate an overall planar dissociation
process with the transition dipole moment μp lying in the
plane and with a ωμp angle (ρ) in the range of 13° to 24°. The J−v correlation varies for each final state and smaller values for χ (ωJ) are interpreted as resulting from out-of-
plane and bending motions of the −NO group in the parent
ground state (“reflection principle”) or from induced “twist” in the dissociation surface (S2) leading to specific
final states.

This study demonstrates the utility of REMPI tech-
niques in determining detailed features of photodissociation
dynamics. The CDAD technique offers a straightforward
means of obtaining initial state alignment. The angular
distribution of REMPI photoions, coupled with CDAD pro-
vide a rather direct description of the angular correlation

between the photolysis transition dipole moment, the photofragment angular momentum and fragment velocity. The advantages offered by these methods include wide applicability of REMPI to molecular systems, relative simplicity of the experimental setup, and a clear-cut data reduction scheme.

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APPENDIX

This section provides a classical derivation of photoion angular distributions resulting from one-photon dissociation followed by a 1 + 1 REMPI probe of the fragment. It is assumed that the dissociation is instantaneous such that the angular distribution reflects the angular relation between the vector quantities \( \mathbf{\mu}_p \), \( \mathbf{J} \), and \( \mathbf{v} \) immediately after photolysis; these quantities were defined in Sec. III C. The derivation will provide expressions for the \( b_0 \), \( b_2 \), and \( b_4 \) parameters of Eq. (20) in terms of the angles \( \rho \) (\( \mu_p \cdot \mathbf{v} \)), \( \chi \) (\( \mathbf{J} \cdot \mathbf{v} \)), and \( \eta \) (\( \mu_p \cdot \mathbf{J} \)). In this derivation it is assumed that the angular distributions characterized by \( \rho \), \( \chi \), and \( \eta \) are for fixed values of these three angles, and do not include a distribution for each angle. However, it is reasonable to expect that photofragments in specific final states will be produced with a range of values in these angles. Therefore, it is more appropriate to interpret any set of \( [\rho, \chi, \eta] \) extracted from experimental data by this procedure as representing an average of each angle over a distribution.

Figure 8 defines two coordinate systems which are relevant to this discussion. The top half of the figure defines coordinates about the center-of-mass of the dissociating system; the photolysis (\( \epsilon_p \)) and fragment absorption (\( \epsilon_f \)) electric vectors are parallel and along the \( z \) axis. The photoions are detected along the velocity vector (of a photofragment) \( \mathbf{v} \) at angle \( \theta \). [The symmetry of the system makes the azimuthal angle \( \phi \) a trivial variable, i.e., \( I(\phi) \propto \cos^2 \phi \) and all quantities employed in deriving it do not depend on \( \phi \).] The lower half of the figure depicts a coordinate system in relation to \( \mathbf{v} \), the axis of detection, about which we define the directions of \( \mathbf{\mu}_p \) and \( \mathbf{J} \) in terms of the angles \( (\rho, \phi^* \) and \( (\chi, \phi') \), respectively. The requirement that \( \eta \) remain fixed imposes a fixed relation between the azimuthal angles \( \phi^* \) and \( \phi' \). Integration about either of \( \phi^* \) or \( \phi' \) averages over all possible orientations of the parent molecule.

The photoion (parent excitation) probability \( |\mu_p \cdot \epsilon_p|^2 \), is proportional to \( k_p = \cos^2 \omega \), where \( \omega \) is the angle between \( \mu_p \) and \( \epsilon_p \). Then \( \omega \) is related to \( \rho \) and \( \theta \) by

\[
\cos \omega = \cos \rho \cos \theta + \sin \rho \sin \theta \cos \phi^*.
\]

If \( \phi' \) is uncorrelated to \( \phi^* \), due to either photolysis mechanism or detection scheme, then the photofragment angular distribution can be obtained by integration of \( k_p \) [the square of Eq. (A1)] about \( \phi^* \) to yield the well known expression \( I(\theta) \propto 1 + \beta P_2(\cos \theta) \), where the parameter \( \beta \) is defined as \( \beta = 2P_2(\cos \rho) \).

However, if the photofragment detection probability depends on the relative orientation of \( \mathbf{J} \) with respect to the probe light polarization \( \epsilon_p \), then a correlation exists between \( \phi^* \) and \( \phi' \). For a one-photon excitation, the transition probability is proportional to \( k_o \), which is given by

\[
k_o \propto E \left( \frac{J + \Delta J}{M_J} \frac{1}{0} \frac{J}{M_J} \right)^2,
\]

where \( E \) are the E1r intensities described in Sec. III A, \( \Delta J \) are 3-j symbols, and \( \Delta J \) is \( -1, 0, \) and \( +1 \) for \( P, Q, \) and \( R \) branch transitions, respectively. The \( M_J \) values are the projections of \( \mathbf{J} \) onto the quantization axis defined by \( \epsilon_p \), such that
\[ M_J = J \cos \alpha, \]
The angle \( \alpha \) is between \( e_p \) and \( J \), and is given in terms of the angles in the coordinate system of Fig. 8:
\[ \cos \alpha = \sin \chi \sin \theta \cos \phi' + \cos \chi \cos \theta. \]  
(A3)
Equation (A2) can be rewritten by substituting explicit expressions for the 3-j symbols:
\[ k_a (P \text{ branch}) = \frac{1}{J(2J+1)(2J+1)} \sin^2 \alpha, \]  
(A4)
\[ k_a (Q \text{ branch}) = \frac{1}{J(2J+1)(J+1)} \cos^2 \alpha, \]  
(A5)
\[ k_a (R \text{ branch}) = \frac{1}{(2J+1)(2J+3)(J+1)} \times [ \sin^2 \alpha + 2J + 1 + J^2 ]. \]  
(A6)
The angle between \( J \) and \( \mu_p, \eta \), imposes a restriction of \( \phi' \) and \( \phi'' \), which is obtained from
\[ \cos \eta = \frac{J \mu_p}{|J| \mu_p} = \sin \chi \sin \rho \cos(\phi' - \phi'') + \cos \chi \cos \rho \]  
(A7)
to yield
\[ \cos(\phi' - \phi'') = \frac{\cos \eta - \cos \chi \cos \rho}{\sin \chi \sin \rho}. \]  
(A8)
We can then rewrite Eq. (A1):
\[ \cos \omega = \cos \rho \cos \theta + \sin \rho \sin \theta \cos(\phi' - \phi'') \cos \phi' + \sin \rho \sin \theta \sin(\phi' - \phi'') \sin \phi'. \]  
(A9)
The angles \( \chi, \rho, \) and \( \eta \) are not completely independent of each other. In fact, given any two, the third must be greater than the difference and less than the sum of the two first:
for a given \( \chi \) and \( \phi' \):
\[ |\rho - \rho| < \eta < (\chi + \rho), \]
for a given \( \rho \) and \( \eta \):
\[ |\rho - \rho| < \eta < (\rho + \eta), \]
for a given \( \eta \) and \( \chi \):
\[ |\eta - \eta| < \rho < (\eta + \chi). \]
The above expressions do not include the angular dependence of the ionization, which is expected to be small, where the ionization light polarization is at angle \( \theta \), from the excitation or photolysis light. If \( \theta \) is constant and does not change with \( \theta \), or if the ionization light is circularly polarized then the ionization has no dependence on \( \theta \).

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37 In Ref. 25 a factor of $(-1)^{4+L} \left( \frac{(2L+1)(2L'+1)}{4\pi} \right)^{1/2} \left( \begin{array}{ccc} L & L' & L \\ 0 & 0 & 0 \end{array} \right)$


39 Table I of Ref. 25 does not explicitly give an expression for $C_{00}$, but it can be easily obtained from $C_{20}$ and the symmetry properties of Eq. (6) of that reference.

40 While this independent experiment can be performed on a gas phase sam-


54 H. Joswig, M. A. O’Halloran, R. N. Zare, and M. S. Child, Faraday Dis-