The Spectroscopy of the CdCH$_3$ Radical and its Positive Ion

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Abstract

Resonantly enhanced multiphoton ionization, REMPI (2 color, 1 + 1$'$), and zero electron kinetic energy-pulsed field ionization, ZEKE-PFI, spectra are reported for the first organometallic radical, CdCH$_3$. The combined REMPI and ZEKE-PFI data have necessitated a change of assignment for one of the bands of the $\tilde{A}^2E \leftarrow \tilde{X}^2A_1$ electronic transition of the neutral radical. The new assignment and the revised molecular parameters are reported. The ZEKE-PFI spectrum yields the adiabatic ionization potential for the CdCH$_3$ radical and four of the six possible vibrational frequencies of its cation. Clearly resolved rotational ($K$ level) structure is observed in some bands of the ZEKE-PFI spectrum, providing a unique experimental test for newly-extended ZEKE-PFI rotational selection rules.

I. INTRODUCTION

Recently there has been a mushrooming$^{1,2}$ of the use of zero-electron kinetic energy-pulsed field ionization (ZEKE-PFI) spectroscopy to investigate the structure of molecular
ions. This technique has generated great excitement because of the detailed knowledge it provides about the ionic states of molecules. However, for the most part, the ions studied have been the cations of closed-shell non-reactive molecules. Nonetheless there have been a few seminal works extending ZEKE-PFI studies to open-shell reactive intermediates. Most notable among these studies are the investigations of the hydroxyl, thiohydroxyl, methyl, benzyl and most recently ammonium radicals.

While existing results are still sparse, the potential for the study of the cations of reactive species is considerable. Many of these cations are key intermediates in a variety of chemical reactions ranging from atmospheric to synthetic organic. We have therefore constructed a ZEKE-PFI apparatus with the principle aim of using it to study reactive chemical intermediates. Our first successful experiments towards that goal have involved organometallic radicals, the metal monomethyls, where the metal belongs to the IIA or IIB group. In this paper, we describe our results for the CdCH₃ radical.

There have been several spectroscopic studies of the cadmium monomethyl radical, CdCH₃, since it was first observed just over two decades ago. A series of experiments on the radical in a free jet environment have determined the vibrational and rotational constants for its \( \tilde{A} \ 2^E \) and \( \tilde{X} \ 2^A \) states. This radical as well as the similar species (ZnCH₃) are of practical importance as they have been shown to be intermediates in a laser-induced metallization process for integrated circuit production. It is also a member of the closely related family of metal methyl radicals whose ions include MgCH₃⁺, prototypical ionic intermediate of synthetic organic Grignard reactions. As reactive intermediates, a thorough knowledge of the spectroscopy of these radicals and their ionic states can be invaluable in investigating reactions in which they play an important role as intermediates.

CdCH₃ was first observed by Young in 1973 in a flash photolysis experiment. In this study they obtained an UV absorption spectrum and assigned two electronic band systems, \( \tilde{A} \ 2^E \leftrightarrow \tilde{X} \ 2^A \) and \( \tilde{B} \ 2^A \leftrightarrow \tilde{X} \ 2^A \), as well as several vibrational frequencies. Subsequent laser induced fluoroscence (LIF) studies on this molecule also reported the same band systems but the rotationally resolved study indicated that most of the features assigned...
to the $\tilde{B}^2A_1 \leftarrow \tilde{X}^2A_1$ system are in fact due to transitions in CdH.

This paper is the first in a series in which we investigate the spectroscopy of the monomethyl family of radicals and their ionic states using the resonantly enhanced multiphoton ionization (REMPI) and ZEKE-PFI techniques. For each of the molecules we will identify the ionization threshold and vibrational frequencies for the ground state of the ion. To effectively obtain this information about the ion using the ZEKE-PFI technique, it is necessary to first understand the spectroscopy of the neutral, particularly its $\tilde{A}^2E$ electronic state which is used as an intermediate state in the $(1 + 1')$ two-photon transition to Rydberg states that are subsequently field ionized to form the cation. Our investigation of the ionization process of CdCH$_3^+$ has led to the reassignment of the $\tilde{A}^2E$ vibrational level, previously thought to be the origin of the $^2E_{3/2}$ spin component, to $\nu_6$ of the $^2E_{1/2}$ spin component. This leaves open the question of the location of the upper $^2E_{3/2}$ spin component. We believe that the answer to this question has recently been provided by an ongoing series of experiments involving fluorescence depletion spectroscopy within our group which attributes the upper spin component of the origin to a feature which is not seen in either the LIF nor the present REMPI studies because of its rapid non-radiative decay.

II. EXPERIMENTAL

The experimental setup has been described elsewhere but a brief summary will be presented here. The CdCH$_3$ radicals were produced from the precursor molecule, cadmium dimethyl, by photolysis with an ArF excimer laser focused by a 50 cm focal length lens to just in front of the nozzle orifice in a supersonic free jet expansion backed by 25-35 psi of He. The flow of He passes over the liquid precursor contained in a stainless steel bomb. The bomb is submerged in a thermostated bath and kept at -5°C. The pulsed supersonic expansion, from a 700$\mu$m nozzle attached to a pulsed valve (General Valve, IOTA One), was skinned by the 1.5 mm skimmer separating the first chamber from the second, high vacuum, ionization chamber. About 10 cm downstream from the skimmer, the molecular
beam passes through the ionization region of the mass spectrometer, consisting of a pair of parallel plates (separation 3 cm). The mass spectrometer used for both the REMPI and the ZEKE-PFI experiments is mechanically the same. The lower plate forming the ionization region acts a repeller accelerating the ions or electrons into a 26 cm flight tube. The detector at the end of the flight tube is a set of microchannel plates. The voltages applied during the two experiments are described below.

For both the REMPI and ZEKE-PFI experiments, the same laser systems were used. As this was a \((1 + 1')\) ionization scheme, two laser beams are produced from a pair of dye lasers (Spectra Physics, PDL-2E and PDL-1) which are pumped by the second and third harmonics of a Nd:YAG laser (Spectra Physics, DCR-2A). The output of one of the dye lasers (PDL-2E), pumped by the third harmonic of the Nd:YAG, was used to excite the neutral radicals to the \(\tilde{A}\ 2\text{E}\) state (excitation laser). The second dye laser beam, pumped by the second harmonic of the Nd:YAG was doubled using a KDP crystal and was used to ionize the radical (ionization laser). The two laser beams pass into the vacuum system through a Brewster window. The arrangement of the laser beams is such that they enter the chamber with a slight angle between them, crossing in the center of the chamber. The path of the two beams was adjusted so that at the center of the ionization region, the two laser beams overlapped temporally.

A Fe/Ne hollow cathode lamp was used to calibrate the fundamental frequency of the ionization laser via the optogalvanic effect. The Fe and Ne lines were less suitable for calibration of the excitation laser due to the congestion of the optogalvanic spectra and significant differences between the optogalvanic and the tabulated emission spectra in this spectral range. Fortunately, very precise, high resolution data on \(\tilde{A} \leftarrow \tilde{X}\) CdCH\(_3\) transitions are available\(^{16}\). Calibration of the excitation laser was verified and corrected using spectral line profiles simulated from the high resolution data. The frequencies reported here are believed to be accurate to ±2 cm\(^{-1}\).

Although the general setup is the same for the REMPI and ZEKE-PFI experiments, the ionization and detection schemes are different. In the REMPI experiment the excitation laser
is scanned through the vibrational levels of the excited electronic state while the ionization laser is kept at a fixed frequency sufficiently energetic to ionize the excited molecules. For detection of ions, a DC voltage of 150 V was applied to the lower plate of the ionization region which accelerated the ions into the flight tube (held at -650 V) and subsequently on to the multichannel plate detector. The resulting signal passed through an AC coupler (present only because it was necessary when detecting electrons and the same detector was used for both ions and electrons) was amplified and sent to a transient recorder (LeCroy TR8818). The signal from the transient recorder was sent to a personal computer, processed, and stored.

In the ZEKE-PFI experiment, the excitation laser is kept at a fixed frequency tuned to a transition between the $\tilde{X}^2A_1$ vibrationless level and a vibronic level of the intermediateCdCH$_3\tilde{A}^2E$ state while the ionization laser was scanned from the ionization energy through the region of interest. In the ZEKE-PFI experiment, the lower plate of the ionization region was pulsed 1 $\mu$s after the ionization laser was fired to a voltage between -0.2 and -10 V. In these experiments the flight tube was held at +150 V and the front of the multichannel plates floated to this same voltage. For these experiments the output of the multichannel plates floated at about 2000 V and it was necessary to send the signal through the AC coupler prior to the preamp. The amplified signal was again sent to the transient recorder and then to the personal computer.

III. THEORY

A. Rotational structure

Although the resolution of this experiment is not sufficient to resolve all of the rotational structure present in the REMPI or ZEKE-PFI spectra, we were able to resolve the $K$ structure in the $e$ vibronic levels of both the $\tilde{A}$ state of the neutral and the $\tilde{X}$ state of the ion. In order to interpret this structure, some understanding of the rotational Hamiltonian
is necessary. A brief description of this rotational Hamiltonians is given below and a more
detailed description can be found elsewhere.\textsuperscript{16,21–23}

The high resolution LIF study\textsuperscript{16} had confirmed that CdCH\textsubscript{3} belongs to the $C_{3v}$ point
group and that the excited and ground states are E and $A_1$, respectively. The rotationally
resolved LIF spectra were analyzed\textsuperscript{16} using a Hamiltonian that was applied to other simi-
lar systems\textsuperscript{21,22} and has been well discussed in the literature\textsuperscript{24,25}. Our description of the
Hamiltonian given here is primarily to identify the interactions and define the molecular
parameters. For CdCH\textsubscript{3}, the effective rotational Hamiltonians for the $\tilde{X}^2A_1$ state, $\mathcal{H}(^2A_1)$,
and for the excited $\tilde{A}^2E$ state, $\mathcal{H}(^2E)$, can be written as

\begin{equation}
\mathcal{H}(^2E) = \mathcal{H}_{\text{Rot}} + \mathcal{H}_{SO} + \mathcal{H}_{\text{Cor}} + \mathcal{H}_{SR} + \mathcal{H}_{JT},
\end{equation}

and

\begin{equation}
\mathcal{H}(^2A_1) = \mathcal{H}_{\text{Rot}} + \mathcal{H}_{SR},
\end{equation}

where $\mathcal{H}_{\text{Rot}}$, $\mathcal{H}_{SO}$, $\mathcal{H}_{\text{Cor}}$, $\mathcal{H}_{SR}$, and $\mathcal{H}_{JT}$ are respectively the rotational, spin-orbit, Corio-
lis, spin-rotation, and Jahn-Teller Hamiltonian terms. All the terms of the Hamiltonian
involve various angular momenta quantities: the total angular momentum of the molecule
(exclusive of nuclear spin) $J$, the electronic spin $S$, the angular momentum of the molecule
without nuclear rotation and electronic spin $N$, the electronic orbital angular momentum
$L$, the vibrational angular momentum $G$ and the (nuclear) rotational angular momentum
$R$. The actual expressions defining the spin-orbit term $\mathcal{H}_{SO}$ ($L$ and $S$ interaction), the
spin-rotation term $\mathcal{H}_{SR}$ ($S$ and $R$ interaction) and the Jahn-Teller interaction term $\mathcal{H}_{JT}$
(involving $L$, $G$, and $R$) are not referred to directly in this work and can be found elsewhere
\textsuperscript{16,21,22,24,25}.

The rotational Hamiltonian is the same for both $^2E$ and $^2A$ states:

\begin{equation}
\mathcal{H}_{\text{Rot}} = AN_Z^2 + B \left(N_X^2 + N_Y^2\right),
\end{equation}

where $A$ and $B$ are the standard prolate symmetric rotor rotational constants.
The Coriolis coupling term is responsible for breaking the degeneracy of the levels with the same absolute value of \( N_Z \) (\( K \) quantum number) due to the interaction between the vibronic angular momentum, \( \mathbf{L} + \mathbf{G} \), and \( \mathbf{N} \). It is written explicitly:

\[
\mathcal{H}_{C_{or}} = -2A (G_Z + L_Z) N_Z = -2A \zeta_t N_Z, \tag{4}
\]

where \( \zeta_t \) is an expectation value of the \( G_Z + L_Z \) operator. The Hamiltonian was used to calculate the rotational structure of the \( \tilde{A} \, ^2E \) intermediate state of neutral \( \text{CdCH}_3 \) as well as the \( \tilde{X}^+ \, ^1A_1 \) state of the ion (in the latter case all the spin interactions being set to zero.)

The software for simulating spectra (\(^2\text{A}\) and \(^2\text{E}\) modules for SpecSim\(^{26}\)) was identical to that used by Cerny et al.\(^{16}\) for their analysis of the rotationally resolved \( \tilde{A} \, ^2E \rightarrow \tilde{X} \, ^2A_1 \) LIF spectra.

**B. Intensity of transitions**

The ZEKE-PFI experiment is a resonant \((1 + 1')\) threshold ionization process. The first step in this process is the \( \tilde{A} \, ^2E \rightarrow \tilde{X} \, ^2A_1 \) excitation in neutral \( \text{CdCH}_3 \). We have taken ZEKE-PFI spectra using several intermediate rovibronic levels of the \( \tilde{A} \, ^2E \) state. The ZEKE-PFI spectra observed using different vibrational levels of the \( \tilde{A} \) state are largely what we would expect using simple Franck-Condon arguments assuming minor changes in the geometry between the \( \tilde{A} \) state of the neutral and the ground \( \tilde{X}^+ \) state of the ion. However, most intriguing are the ZEKE-PFI spectra involving transitions from the \( e \) vibrational level \( v_6 = 1 \) in the \( \tilde{A} \) state to \( v_6 = 1 \) in the ion. These spectra show clearly resolved \( K \) structure in the ion, which markedly changes as different rotational levels are used in the intermediate \( \tilde{A} \) state.

Obtaining the selection rules and relative intensities for these transitions is a complex problem; fortunately there is a good theoretical foundation upon which to build. Recently, we\(^{23}\) have worked out in some detail the transition probabilities for \( a - e \) and \( e - e \) bound-bound vibronic transitions in the analogous \( C_3v \) molecules \( \text{CH}_3\text{O} \) and \( \text{CF}_3\text{O} \). Müller-Dethlefs\(^{27,28}\) has considered in detail the rotational selection rules and intensities in the
ZEKE-PFI spectra of molecules with $C_{\infty v}$ symmetry (NO) and $D_{3h}$ symmetry (NH$_3$). By combining these results we are able to explain rather satisfactorily the observed ZEKE-PFI spectra.

Before expounding upon the detailed theory of the transitions a few words about nomenclature are in order. The ZEKE-PFI experiments start with CdCH$_3$ in its $\tilde{A}^2A_1$ state whose “rotational” quantum numbers will be denoted by double primes, e.g., $J''$, $K''$, $M''$, etc. The intermediate state in the experiment is the $\tilde{A}^2E$ state whose rotational quantum numbers will be denoted by single primes, e.g., $J'$, $K'$, $M'$, etc. The terminal state of the ZEKE-PFI experiment is an electron plus the ground $\tilde{X}^+1A_1$ state of CdCH$_3^+$, whose rotational quantum numbers are denoted by superscript pluses, e.g., $J^+$, $K^+$, $M^+$, etc.

The key to understanding the rotational structure of the ZEKE-PFI spectra lies in the transition dipole matrix element between the $\tilde{A}^2E_1$ $v_6 = 1$ level and the $v_6 = 1$ of Rydberg state with ion core, $\tilde{X}^+1A_1$ where it should be remembered that $v_6$ is a vibration of $e$ symmetry. Extending the argument of Müller-Dethlefs we write the Rydberg state wavepacket as

$$
\left| \tilde{X}^+e_{\pm}, N^+K^+M^* \right> = \sum_{n^*,N^*,l_R} a_{n^*,N^*,l_R} (-1)^{N^*-\lambda_R+K^+} \left( 2N^+ + 1 \right)^{1/2} (5)
$$

$$
\times \begin{pmatrix} N^+ & l_R & N^* \\ K^+ & \lambda_R & -K^* \end{pmatrix} \left| \tilde{X}^+e_{\pm} \right> \left| N^* K^* M^* \right> \left| l_R \lambda_R \right>
$$

where the quantity enclosed by large parentheses is a 3-j symbol.

The sum over $n^*$, $N^*$, $l_R$ includes all eigenfunctions appropriately weighted by coefficients, $a_{n^*,N^*,l_R}$, that are excited by the “ionization” laser pulse and hence contribute to the wavepacket. The sum over $K^*$, $\lambda_R$ allows the combination of the ion core and Rydberg functions into a case (d) like coupling scheme which has $N^* = N^+ + l_R$, where it must be remembered that $N^*$ and $N^+$ obey reversed commutation relations in the molecule-fixed coordinate system. The ket $\left| N^* K^* M^* \right>$ represents a symmetric rotor basis function for the angular momentum $N^*$ with projections $K^*$ and $M^*$ in the molecule and space fixed coordinate system respectively. The atomic-like Rydberg orbital is denoted $\left| l_R \lambda_R \right>$ with electronic
angular momentum $l_R$ and projection along the $C_3$ axis, $\lambda_R$. The kets $|\tilde{X}^+ e_\pm\rangle$ are the vibronic basis functions for the ground state cation in $v_6 = 1$. Under the $C_3$ rotation of $C_{3v}$

$$C_3 |\tilde{X}^+ e_\pm\rangle = e^{\mp i/3} |\tilde{X}^+ e_\pm\rangle$$  \hfill (6)

To calculate the transition matrix element, it is useful to construct the symmetric/antisymmetric linear combinations of the wavefunctions, which are eigenfunctions (with eigenvalues $p = \pm 1$) of the xz reflection, $\sigma_{xz}$, of the $C_{3v}$ group. We note that

$$\sigma_{xz} |\tilde{X}^+ e_\pm\rangle |N^* K^* M^*\rangle |l_R \lambda_R\rangle = (-1)^{N^* - K^* + l_R - \lambda_R} |\tilde{X}^+ e_\pm\rangle |N^*, -K^*, M^*\rangle |l_R, -\lambda_R\rangle$$  \hfill (7)

and therefore define symmetrized basis functions as

$$|\tilde{X}^+ e, N^* K^* N^* M^*\rangle = |\tilde{X}^+ e_+, N^* K^* N^* M^*\rangle \pm (-1)^{N^* - K^*} |\tilde{X}^+ e_-, N^* - K^* N^* M^*\rangle$$

$$= \frac{\sqrt{2N^* + 1}}{\sqrt{2}} (-1)^{K^*} \sum_{n^* K^*} (-1)^{N^* - \lambda_R} a_{n^*, N^* l_R} \left(\begin{array}{ccc}
N^* & l_R & N^* \\
K^* & \lambda_R & -K^*
\end{array}\right)$$

$$\times |\tilde{X}^+ e, l_R \lambda_R, N^* K^* M^*\rangle,$$  \hfill (8)

where

$$|\tilde{X}^+ e, l_R \lambda_R, N^* K^* M^*\rangle$$

$$= |\tilde{X}^+ e_+\rangle |N^* K^* M^*\rangle |l_R \lambda_R\rangle \pm (-1)^{N^* - K^* + l_R - \lambda_R} |\tilde{X}^+ e_-\rangle |N^* - K^* M^*\rangle |l_R - \lambda_R\rangle$$  \hfill (9)

In our calculation of the transition moment, we note that the spin-structure is not resolved in the ground state of the ion, hence we have neglected spin in our basis set for simplicity. Inclusion of spin would not alter our results because of the selection rule for the spin projection, $\Sigma$, on the $C_3$ axis of $\Delta \Sigma = 0$ for the electric dipole transitions.

The corresponding symmetrized basis function for the $v_6 = 1$ level of the intermediate $\tilde{A}$ state is defined in the usual way,

$$|\tilde{A} e, N K M \pm\rangle = \frac{1}{\sqrt{2}} \left( |\tilde{A} e_+\rangle |N K M\rangle \pm (-1)^{N-K} |\tilde{A} e_-\rangle |N -K M\rangle \right)$$,  \hfill (10)
where the $|\tilde{A}e_{\pm}\rangle$ are vibronic eigenfunctions of symmetry species $e$ and transform analogously to $|\tilde{X}^+e_{\pm}\rangle$.

The intensity of transitions to Rydberg states of particular rotational levels of the ion core are determined by evaluating the square of the electric dipole transition matrix element between states represented by Eqs. (8) and (10). This evaluation is performed in the Appendix where after tedious manipulation, we are able to express the result in terms of a Hönl-London-like line strength factor, $S$, where

$$S \left( eN^+K^+p; e'N'K'p' \right)$$

$$= \delta_{p,-p} (2N^+ + 1)(2N' + 1) \sum_{l_A, \lambda_A=1,-2,4,-5,...} a_{l_A}^2 A_{l_A} \begin{pmatrix} N^+ & l_A & N' \\ -K^+ & -\lambda_A & -K' \end{pmatrix}^2,$$

with $a_{l_A}$ and $A_{l_A}$ defined in Eqs. (A5) and (A15). As shown in the Appendix the sum over $l_A$ in principle runs over all atomic states, but for an $e$ vibronic state, symmetry restricts the only allowed values of $\lambda_A$ to those that satisfy the equation,

$$\lambda_A = -(3n+2) = -2, +1, -5, +4...$$

Indeed if we only consider $s$, $p$, and $d$ functions then the only contributing atomic orbitals, $(l_A, \lambda_R)$, are $(1, 1)$, $(2, 1)$ and $(2, -2)$. If we now combine this result with the rule for the non-vanishing of the 3-j symbol in Eq. 11, we have the following selection rules for the ionizing transitions from the $\tilde{A}^2E$, $v_0 = 1$ intermediate level in CdCH₃,

$$K^+ + K' = -\lambda_A = -1 \ (p \ orbital)$$

$$K^+ + K' = -\lambda_A = -1 \ or \ 2 \ (d \ orbital)$$

Since the $\tilde{A}$ state is fairly well represented by the $p$ orbital, the strongest transitions would be expected to be governed by Eq. 13, with weaker transitions allowed by Eq. 14.
IV. RESULTS AND DISCUSSION

The energy necessary to directly ionize CdCH$_3$ is large enough to require a vacuum ultraviolet photon. To avoid this complication, a resonant two photon process was utilized with the vibrational levels of the $\tilde{A}^2E$ electronic state of the neutral CdCH$_3$ as intermediate states. In addition to the simplification of not having to work in the vacuum ultraviolet region the two photon process has the added advantage that it enables one to have confidence that the ZEKE-PFI signal is from the correct species. In any photolytic dissociation process forming a radical species of interest, it is possible to have unwanted by-products. These other species can complicate the detection and determination of the spectral features from the desired product, and in the worse case lead to an incorrect attribution of the carrier. In the $(1+1')$ detection scheme, one can virtually ensure the detection of the desired species if the first photon is on resonance with a known transition of the radical species of interest. A further advantage of the $(1+1')$ ionization approach, which will be demonstrated for CdCH$_3$, is the capability of going through different intermediate states. This approach greatly aids the assignment of the vibronic nature of the neutral intermediate levels and the final vibronic states of the ion.

A. REMPI Spectrum of CdCH$_3$

In order to effectively utilize the $\tilde{A}^2E$ state of CdCH$_3$ as an intermediate level for the ZEKE-PFI spectrum of its cation, it is important to understand the vibrational structure of this state. To this end the $(1+1')$ REMPI spectrum of CdCH$_3$ was obtained and is shown in Fig. 1. As with other C$_3v$ molecules, CdCH$_3$ has six normal modes, three totally symmetric $a_1$ and three degenerate $e$ vibrations. Of these six vibrations, only those vibrations of $a_1$ symmetry are formally allowed in an $E\leftarrow A_1$ electronic transition although the $e$ vibrations can become allowed due to the Jahn-Teller interaction in the excited state. In the REMPI spectrum in the cold jet all transitions originate from the vibrationless level of the $\tilde{X}$ state.
of CdCH₃, and all the previously reported laser induced fluorescence (LIF) bands are present. In addition to the \( \tilde{A} \ ^2E_{1/2} \) component of the origin (22514 cm\(^{-1}\)), we see two strong bands due to excitation of the totally symmetric modes \( \nu_2 \) (23533 cm\(^{-1}\)) and \( \nu_3 \) (22915 cm\(^{-1}\)) which are, respectively, the CH₃ umbrella and Cd-C stretch mode. These band assignments have been given previously.

A band (≈ 23164 cm\(^{-1}\)) is also seen in the REMPI spectra which was previously assigned in the LIF spectra as the \( \tilde{A} \ ^2E_{3/2} \) component of the \( \tilde{A} \ ^2E \leftarrow \tilde{X} ^2A_1 \) origin. We have now reassigned this band as the \( \tilde{A} \ ^2E_{1/2} \) component of the \( 6^1 \) transition. This \( e \leftarrow a_1 \) transition is allowed because of the Jahn-Teller affect in the \( ^2E \) state. The previous assignment of this band as the \( \tilde{A} \ ^2E_{3/2} \) component of the origin was made in part because of the need to assign a feature to the upper spin component of the origin. This assignment was justified by a rotational analysis but in order to fit the data it was necessary to apply an unusually large spin-rotation coupling constant, \( \epsilon_{aa} \), of 474 GHz. This value is anomalously large compared with similar molecules, a fact previously explained by presuming the existence of a perturbing electronic state.

The current reassignment of this band as \( 6^1 \) is based predominately upon the experimental data obtained in the present ZEKE-PFI studies but this assignment is consistent with \textit{ab initio} calculations (see Table III). As will be discussed in more detail in section IV B, the ZEKE-PFI transitions observed when \( 6^1 \) is used as an intermediate state all result in excitation of \( \nu_0 \) in the ion. These results are shown quite clearly in trace (c) of Fig. 2. This is quite different from the observed ZEKE-PFI transitions seen using the \( \tilde{A} \ ^2E_{1/2} \) origin (trace a) as the intermediate state whereas one would expect the ZEKE-PFI spectra using the two spin orbit components of the origin to be quite similar. Furthermore, as Fig. 2 shows, the ZEKE-PFI spectra via any of the totally symmetric levels as intermediate states appear mainly to only excite the corresponding mode in the ion, giving support to the assignment of the feature at 23164 cm\(^{-1}\) as the \( \tilde{A} \ ^2E_{1/2} \) component of the \( 6^1 \) transition.

The reassignment of the feature previously believed to be the origin of the \( \tilde{A} \ ^2E_{3/2} \) electronic state to \( \tilde{A} \ ^2E_{1/2} \ ^6 \) raises two important questions. Is the rotational structure,
which has already been shown to be consistent with the origin of the \( \tilde{A} \ ^2E_{3/2} \) electronic state, also consistent with a transition to \( \tilde{A} \ ^2E_{1/2} \ 6^1_0 \), and if this is \( 6^1_0 \), where is the upper spin component of the origin?

To verify that a good fit to the rotational structure could be achieved, the following analysis was performed. Since the apparatus used for these experiments does not have sufficient resolution to obtain a completely rotationally resolved scan, a trace of the rotational features of the band of interest was generated using the rotational constants from the previous work\(^{16}\). This trace was then fit with constants consistent with a transition to the \( \tilde{A} \ ^2E_{1/2} \ 6^1_0 \) level. Table II lists the rotational constants used for the simulation\(^{16}\) and the final constants from the fit. Several points should be made about this table. First, since we can only identify one of the spin orbit components, we have no real value for the spin orbit coupling constant \( A_{e}d \) but we still assume that it is large enough to cleanly separate the two spin orbit components. Since \( 6^1 \) has \( e \) vibronic symmetry, there is a non-zero value in \( \mathcal{H}_{Cor} \) for the Coriolis coupling parameter, \( \zeta \), where \( \zeta \) is the expectation value of the \( G_Z + L_Z \) operator. The vibrational contribution significantly changes the value of \( A_{\zeta} \) from that\(^{16}\) of the origin of the \( \ ^2E_{1/2} \) state, where sans Jahn-Teller coupling, \( G_Z \) vanishes. For this simulation, since only one spin orbit components is observed, we have set the values of \( a_D \zeta_e d \) and \( \epsilon_{aa} \) to zero. With the constants listed in Table II we were able to obtain an equivalent fit to the rotationally resolved data while using the effective Hamiltonian appropriate to the \( \tilde{A} \ ^2E_{1/2} \ 6^1 \) level. Indeed it may be argued that the \( 6^1 \) effective \( \mathcal{H} \) is preferable since none of its parameters have anomalous values, requiring unindentified perturbing states for their explanation.

Despite the drastic change in the vibrational assignment, the assignment of the rotational substructure of the band remains unchanged. Thus, it is possible to distinguish five rotational sub-bands with \( K' = 0, -2, -3, 1, \) and \( 2 \), as previously identified. Figure 3 shows this band in the observed REMPI spectrum with the \( K' \) levels identified. (The numbers in parenthesis indicate the \( K' \) levels admixed by terms of \( \mathcal{H}_{SR} \) and \( \mathcal{H}_{JT} \) –see below.)
We also feel that we now have an answer to the nagging question of where the \( ^2E_{3/2} \) component of the origin is. Another study on this molecule using the fluorescence depletion technique\(^{19}\) to investigate optically dark states of molecules has shown that there exists a number of dark levels in the region where the upper spin component of the origin is expected. In fact, we now believe the \( ^2E_{3/2} \) component of the origin to be at 23422 cm\(^{-1}\) and that it is not observed in the LIF or REMPI studies because of a rapid, non-radiative decay.

\[ \text{B. ZEKE-PFI spectroscopy of the CdCH}_3 \text{ Cation} \]

ZEKE-PFI spectra of CdCH\(_3\) were recorded via the following \( \tilde{A} \ ^2E_{1/2} \) vibrational levels: the vibrationless level, \( 3^1 \), \( 2^1 \) and the five resolved \( K' \) components of the \( 6^1 \) level as shown in Fig. 3. For each of the transitions pumped, the excitation laser has been tuned to the center of the REMPI peak. The transition frequencies relative to the vibrationless level of the \( \tilde{X} \ ^1A_1 \) state of the ion are listed in Table I. Each of the spectra will now be briefly described.

1. ZEKE-PFI Spectra the \( \tilde{A} \ ^2E_{1/2} \) origin and the adiabatic ionization energy (AIE)

Trace (a) of Fig. 2 shows the ZEKE-PFI spectrum obtained using the origin of the \( \tilde{A} \ ^2E_{1/2} \) state as an intermediate level. Numerous transitions to excited vibrational levels of the ion are observed and described below. However as one can easily see from Fig. 2, the strongest transition is to the origin of the \( \tilde{X} \) state of the ion. This very strong transition was used to determine the AIE of CdCH\(_3\).

In theory, ZEKE-PFI can yield very accurate ionization energies limited, in the best case, by the bandwidth of the lasers used. There are however other complicating factors. In the presence of an electric field the ionization energy is shifted\(^{30,20,31}\) between \( 4\sqrt{F} \) (diabatic) and \( 6\sqrt{F} \) (adiabatic) where \( F \) is the applied field in V cm\(^{-1}\). By varying the field strength one can extrapolate to zero field and obtain a better estimate of the ionization energy\(^{20}\) although better techniques\(^{32}\), such as utilization of a pulse with a slow rise or multi step
extraction pulses, have been developed to improve on the measurement. In the present study
the electric field was varied from 0.5V to 10 V over a 3 cm gap of the ionization region. There
was no measurable shift or broadening of the ZEKE-PFI peak as the extraction voltage was
varied. Most likely, the lack of a measurable shift is due in part to the width of the features
(about 8 cm$^{-1}$), which is limited primarily by unresolved rotational structure, and by the
fairly narrow range for which the electric field strength was varied. By taking the center of
the rotational contour of the ZEKE-PFI signal, the AIE of CdCH$_3$ was determined to be
57105(6) cm$^{-1}$.

2. ZEKE-PFI Spectra via the $\tilde{A}$ $^2E_{1/2}$ $a_1$ vibrational levels

The ZEKE spectra from the vibrationless level (discussed above) of the $\tilde{A}$ $^2E_{1/2}$ state and
with one quanta of either the $\nu_3$ or $\nu_2$ totally symmetric modes are presented in Fig. 2(a, b, d).
The frequency axis in this figure represents the total energy from the vibrationless level of the
ground state of the neutral CdCH$_3$. These values were obtained by adding the frequencies of
the excitation and ionization lasers. Each of the spectra is dominated by the vibrationally
diagonal transition, which indicates that there is a relatively small change in geometry
between the $\tilde{A}$ $^2E_{1/2}$ state and the ground state of the ion. As may be seen, the transition
to the origin is the strongest feature in the spectrum when the origin of the $\tilde{A}$ state of the
neutral is used as the intermediate level. It is also seen, with greatly diminished intensity,
in the spectrum taken via the $\tilde{A}$ $^2E_{1/2}$ $\nu_2$ state. There is no observable feature at the origin
in the spectrum recorded via the $\tilde{A}$ $^2E_{1/2}$ $\nu_3$ band.

Spectra taken via both the origin and $\nu_2$ contain broad, asymmetrically shaped bands
which we assign to $\nu_6$ (57852 cm$^{-1}$) and combination bands (58272 and 58951 cm$^{-1}$)
involving this mode in the ion. The band at 58500 cm$^{-1}$ in the ZEKE-PFI spectrum taken
via the origin has a shape similar to the $\nu_6$ band but cannot be assigned to any combination
or overtone band that involves the $\nu_6$ mode. It is therefore assigned to a transition to $\nu_5$,
another $e$ symmetry mode. The assignment of this feature as $\nu_5$ is also consistent with the
calculations of the mode’s frequency (see Table III). Also observed in the ZEKE-PFI spectra through the origin of the intermediate state are a couple features (58596 and 59008 cm\(^{-1}\)) terminating on levels involving the \(6^2\) overtone in the ion. The experimentally determined frequencies for four (\(\nu_2, \nu_3, \nu_5, \nu_6\)) of the 6 vibrational modes of the ion are given in Table III.

3. ZEKE-PFI Spectra via the \(\tilde{A}^2 E_{1/2} \nu_6\) vibrational level.

As shown in Fig. 2(c), when the mode now assigned as \(\nu_6\) in the intermediate \(\tilde{A}^2 E_{1/2}\) state is excited, the bands associated with \(\nu_6\) in the ion become dominant features in the ZEKE-PFI spectrum. In trace (c) (taken via the \(K' = 2\) level), there is a small, yet observable peak terminating at the origin as well as at the \(\nu_6\) and \(2\nu_6\) bands and the \(\nu_3 + \nu_6\) combination levels of the \(\tilde{X}^2 A_1\) state of the ion. Moreover we note from Fig. 2(c) that bands containing \(\nu_6\) motion in \(\text{CdCH}_3^+\) have structure which we attribute to internal \(K^+\) levels in the ion.

The additional presence of \(K'\) sub-bands in the \(\tilde{A}^2 E_{1/2} \ 6^1_0\) band of the \(\text{CdCH}_3\) neutral provides a unique opportunity to probe different \(K^+\) sub-levels of the ion via excitation of different \(K'\) levels in the \(\nu_6\) mode in the intermediate \(\tilde{A}^2 E\) state. An expanded view of the \(6^1\) region of the ZEKE-PFI spectra via different \(K'\) levels is shown in Fig. 5. The internal \(K^+\) structure of the \(\nu_6\) and \(\nu_3 + \nu_6\) bands of the ion are similar and undergo the same transformation as the \(K'\) value of the intermediate level is changed. That is expected behavior, because these respective vibrational levels differ only by one quantum of the symmetric mode \(\nu_3\). The \(2\nu_6\) band has a different internal structure but also changes with the \(K'\) value of the intermediate level.

The structure observed in the ZEKE-PFI spectrum can be understood in terms of the selection rules derived in Section III B. We expect the ionized electron to be located in the \(\tilde{A}^2 E\) intermediate state of the \(\text{CdCH}_3\) in an orbital that is reasonably well approximated by a \(p\) atomic orbital localized on Cd, with some admixture of \(d\) character. Ergo, we expect from Section III B that the strong ZEKE-PFI transitions will be governed by the selection
rule, \( K^+ + K' = -1 \). Turning to Fig. 5 we see that the expectation is borne out for the ZEKE-PFI spectrum taken from each of the 5 distinct \( K' \) states excited. Indeed the strongest transition in each of the ZEKE-PFI traces obeys this selection rule. (The sixth \( K' \) state, \( K' = -1 \), is not resolved in the REMPI spectrum of Fig. 3, although it has been observed in the LIF spectrum as a weak shoulder on the low-frequency side of the transition to \( K' = 0 \).)

There are however other, weaker transitions present in each of the traces of Fig. 5. There are two expected reasons for the breakdown of the above selection rule and we examine these in turn. We know that \( K' \) is not a good quantum number in the \( \tilde{A} \) state or else we would never have observed transitions to \( K' = -2 \) and \( -3 \) in the REMPI and LIF spectrum of the \( \tilde{A} - \tilde{X} \) transition. In CdCH\(_3\) \( \tilde{A}^2E_{1/2} \nu_6 \) level (as described elsewhere\(^\text{16} \)) there is mixing of the \( K' \) levels by terms of \( \mathcal{H}_{SR} \) and \( \mathcal{H}_{JT} \), involving the \( h_2 \) and \( \epsilon_{2a} \) parameters. This interaction mixes levels with the quantum number \( P' \) with \(-P'\), or in terms of \( K' \), where \( K' = P' - \Sigma', K' \) with \(-K' - 1\). This mixing means that where we label a level \( K' \), this level actually contains some \(-(K' + 1)\) character. For example, the level \( K' = 2 \) is mixed with the level \( K' = -3 \) giving it the character of both these levels and ergo transitions from this level would be expected to have allowed transitions consistent with both \( K' = 2 \) and \( -3 \). Indeed the mixed \( K' \) character of each of the intermediate \( \tilde{A} \) state levels is indicated in Fig. 3 showing the REMPI spectrum of CdCH\(_3\). Still using the \((K^+ + K' = -1)\) selection rule, but now inserting the admixed value of \( K' \) (given in parenthesis in Fig. 3), we predict a satellite transition for each first-order allowed ZEKE-PFI transition and Fig. 5 shows that in every case a weaker transition is observed at the predicted location.

At this point in the analyses all but two of the observed transitions in the 5 traces of Fig. 5 are accounted for. The extra feature at 57880 cm\(^{-1}\) in the bottom, \( K' = -3 \) trace of Fig. 5 has a relatively trivial explanation. This feature is present because we do not have adequate resolution between the transitions to the \( K' = 1 \) and \( K' = -3 \) levels. Because of this, when our first laser is at the frequency of the transition to \( K' = -3 \), we also drive significant population to the high \( J \) levels of the \( K' = 1 \) state which overlaps in frequency.
Therefore we see transitions to the ion from the $K' = 1$ level, which by the above selection rule gives a transition to $K^+ = -2$, as indicated in Fig. 5.

The final transition to be explained is that from $K' = 2$ to $K^+ = 0$ in the top trace of Fig. 5. For its explanation we turn to the $d$ atomic wavefunction participation in the molecular orbital (in the $\tilde{A}$ state) of the ionized electron. Section III B predicts an additional selection rule for the $d$ orbital contribution of $K^+ + K' = 2$. We note that this rule predicts the observed transition from $K' = 2$ to $K^+ = 0$. For the next trace for $K' = 1$ the same selection rule predicts a transition to $K^+ = 1$, which is observed, but as we saw above, is also allowed by $K'$ mixing. For the smaller values of $K'$, transitions are predicted to higher $K^+$ levels, but none of these are actually observed. This is not particularly surprising. For the $K' = 0$ trace this transition may be of lower intensity than the relatively weak ones observed to $K^+ = 0$ and 1, and could easily be below the experimental signal/noise level. For the $K' = -2$ and $-3$ traces, the additional transition is off the scale of the frequency scan.

Moreover further support for the existence of a small, but not negligible $d$ orbital participation, can be gleaned from the ZEKE-PFI spectrum of the closely related ZnCH₃, whose analysis is near completion. In this case $K'$ mixing is effectively absent in the $\tilde{A}$ intermediate state so that ZEKE-PFI transitions are observed only from $K' = 2$, 1 and 0. The traces obtained for ZnCH₃ again clearly show transitions in the ZEKE-PFI spectra allowed by $d$-orbital character but show no clear evidence for those allowed by only $K'$ mixing.

The predicted bands in Fig. 5 have been simulated using a rotational temperature of $T=10$K and were convoluted by a 4 cm⁻¹ Gaussian profile representing the instrumental resolution of the ZEKE-PFI experiment. The relative intensities of the satellite lines in each trace have been adjusted to match the experimental results. The precise positions of the bands were simulated using the known $K'$ structure of the $\tilde{A}$ state and allowing modest variation in the rotational and Coriolis constants of the $\tilde{X}^+$ state of CdCH₃.

The simulation and fitting of the $K^+$ structure in the $\nu_6$ bands of the ion was again done with the SpecSim program. The standard doublet symmetric rotor model, $\mathcal{H}_{Rot} + \mathcal{H}_{Cor}$,
was modified and a set of parameters was added to it to allow control of the lower state \( K' \) relative population. For the simulations, only a single \( K' \) level, of the \( \tilde{A} \ ^2E_{1/2} \nu_6 \) state, \( K' = 0, 1, -2, 2 \) or \(-3 \) level was populated. The \( \tilde{A} \ ^2E_{1/2} \nu_6 \) state constants used were those listed in Table II. Least square fitting was used to determine the parameters of the \( \tilde{X}^+ \) state of the ion and produce the simulated ZEKE-PFI traces. For the \( \tilde{X}^+ \) state of the ion we obtain the results \( A - B = 5.0(1) \) and \( A\zeta_t = 0.4(2) \) cm\(^{-1}\), both values being consistent with expectations based upon the \( \tilde{A} \) and \( \tilde{X} \) states of neutral CdCH\(_3\).

**V. CONCLUSIONS**

The first ZEKE-PFI spectrum of any organometallic radical is reported. The combined analysis of the ZEKE-PFI and the REMPI spectrum of CdCH\(_3\) provides new information about both the \( \tilde{A} \ ^2E \) state of neutral CdCH\(_3\) as well as the \( \tilde{X}^+ \ ^2A_1 \) state of its cation. With respect to the neutral, the observations lead us to re-assign the transition at 23150 cm\(^{-1}\) in the \( \tilde{A} \ ^2E - \tilde{X} \ ^2A_1 \) electronic spectrum. Based upon the combined ZEKE-PFI and REMPI data, we now believe the terminal level to be \( \nu_6 = 1 \) of the \( ^2E_{1/2} \) spin-component of the \( \tilde{A} \) state, not the vibrationless level of the \( ^2E_{3/2} \) spin component as previously reported. This leads to the re-evaluation of a couple of molecular parameters for the \( \tilde{A} \) state, with, we believe, more physically satisfying results.

The ZEKE-PFI spectrum allows the AIE energy of CdCH\(_3\) to be precisely determined. In addition four of the six possible vibrational modes of the ion have been observed and their frequencies obtained. Comparison of these frequencies with those of the \( \tilde{A} \) and \( \tilde{X} \) states of the neutral as well as to \textit{ab initio} calculations have been made.

Clearly resolved \( K \) rotational structure has been observed in \( \nu_6 = 1 \) for both the neutral \( \tilde{A} \) state and the \( \tilde{X}^+ \) state of the ion. These results offer a unique test of our understanding of the “rotational selection rules” in ZEKE-PFI spectroscopy. We have extended the previous theoretical formulation of the selection rules to cover the observed transitions. We find good agreement between our observations and the theoretical predictions.
The present experiments have demonstrated the ability to obtain experimentally ZEKE-PFI spectra, with both good signal/noise and resolution, for an organometallic radical species. We are in the process of extending our observations to other metal methyl radicals as well as to other complex chemical intermediates.

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APPENDIX A: SYMMETRIC ROTOR LINE STRENGTH FACTORS

The intensity of the transitions between the $\tilde{A}^2E$, $\nu_0 = 1$ intermediate state and the Rydberg state with ion core, $\tilde{X}^+$, $\nu_0 = 1$ is determined by two factors: the population of the lower level and Hönl-London-like line strength factors $S(eN^+K^+; e'N'K')$. The population of the ground state levels is either determined by the Boltzman distribution and the nuclear spin statistical weight$^{22,17}$ or if necessary, controlled by the parameters of the model for a non-statistical distribution. The line strength factors are determined by the matrix elements of the dipole moment operator evaluated between the ground and excited state vibronic wavefunctions.

The line strength $S(eN^+K^+; e'N'K')$ is defined in the usual way, namely,

$$S(eN^+K^+; e'N'K') = \sum_{M^*, M'} \left| \langle N^+K^+M^* | \mu_Z | N'K'M' \rangle \right|^2$$

(A1)

where $\mu_Z$ is the zeroth component of the first order spherical tensor $\mu$ in a space-fixed-frame. The space and molecule fixed frames are related by a rotation through Euler angles $\omega$, so

$$\mu_Z = \sum D_{0q}^1 \mu_q,$$

(A2)

where $\mu_q$ are the components of $\mu$ in the molecule-fixed-frame.

Then the expression for the line strength factor is

$$S(eN^+K^+; e'N'K') = 3 \sum_{M^*, M'} \left| \sum_q \left( \langle \tilde{X}^+e, N^+K^+M^* | D_0^1 e^* (\omega) \mu_q | \tilde{A}e, N'K'M' \rangle \right) \right|^2$$

(A3)

$$= 3 \sum_{M^*, M'} \sum_{q, N^*, K^*, l_R, \lambda_R} a_{N^*, K^*, l_R, \lambda_R} \left( \langle \tilde{X}^+e, l_R\lambda_R, N^*K^*M^* | D_0^1 e^* (\omega) \mu_q | \tilde{A}e, N'K'M' \rangle \right)^2,$$

where the coefficient, $a_{N^*, K^*, l_R, \lambda_R}$, in accordance with Eq. (8) is given by

$$a_{N^*, K^*, l_R, \lambda_R} = a_{N^*, l_R} \frac{(-1)^{N^*+K^+ - \lambda_R}}{\sqrt{2}} \frac{1}{\sqrt{2N^* + 1}} \begin{pmatrix} N^+ & l_R & N^* \\ K^+ & \lambda & -K^* \end{pmatrix}$$

(A4)

We can, using $|\tilde{A}_{cor}\rangle$ as the notation for the closed-shell core of the $\tilde{A}$ state, approximate the vibronic eigenfunctions of both the intermediate $\tilde{A}$ and Rydberg states in a similar manner:
\[ |\tilde{A}, \nu_6 = 1\rangle = \sum_{l_A, \lambda_A} a_{l_A} |\tilde{A}_{\text{cor}}\rangle |\nu'_6 = 1\rangle |l_A, \lambda_A\rangle \]  
\[ |\tilde{X}^+, \nu_6^+ = 1, l_R\lambda_R\rangle = \sum_{\lambda_R} |\tilde{X}^+\rangle |\nu_6 = 1\rangle |l_R, \lambda_R\rangle \]

To evaluate the matrix elements of the \( D_{0q}^1(*) \mu_q \) operator in the symmetrized basis set defined by Eqs. (8) and (10) it is convenient to present the rovibronic states of both \( A_1 \) and \( E \) vibronic symmetry in a uniform way:

\[ |NKM\pm\rangle = \frac{|\gamma_1\rangle |NKM\rangle \pm (-1)^{N-K} |\gamma_2\rangle |N-KM\rangle}{\sqrt{2}} \]  
\[ (A5) \]

where \( \gamma_1 \) and \( \gamma_2 \) label the vibronic wavefunctions and are defined by

\[ |\gamma_1\rangle = \sum_{l_A, \lambda_A=1, -2, 4, -5} a_{l_A} |\tilde{A}_{\text{cor}}\rangle |\nu_6 = 1, l = -1\rangle |l_A, -\lambda_A\rangle \]  
\[ (A7) \]

\[ |\gamma_2\rangle = \sum_{l_A, \lambda_A=1, -2, 4, -5} a_{l_A} (-1)^{l_A+\lambda_A} |\tilde{A}_{\text{cor}}\rangle |\nu_6 = 1, l = 1\rangle |l_A, \lambda_A\rangle \]

\[ |\gamma_1^+\rangle = |\tilde{X}^+\rangle |\nu_6 = 1, l = 1\rangle |l_R, \lambda_R\rangle \]

\[ |\gamma_2^+\rangle = (-1)^{l_R+\lambda_R} |\tilde{X}^+\rangle |\nu_6 = 1, l = -1\rangle |l_R, -\lambda_R\rangle \]

where we have restricted the run over \( \lambda_A \) such that the overall vibronic state has \( e \) symmetry. No similar restriction exists on the run over \( \lambda_R \) in Eq. (1), since only the vibronic symmetry on the ion core is known, not that of the Rydberg state.

Using this notation the matrix elements of \( D_{0q}^1(*) \mu_q \) can be evaluated in a straightforward manner:

\[ \langle \Gamma^+, N^*K^*M^* \pm \rangle D_{0q}^1(*) \mu_q |\Gamma', N'K'M'\mp \rangle \]  
\[ (A8) \]

\[ = \langle \gamma_1^+ |\mu_q |\gamma_1\rangle \langle N^*K^*M^* | D_{0q}^1(*) \omega |N'K'M'\rangle \]

\[ \mp \langle \gamma_1^+ |\mu_q |\gamma_2\rangle \langle N^*K^*M^* | D_{0q}^1(*) \omega |N'K'M'\rangle (-1)^{N'-K'} \]

\[ \pm \langle \gamma_2^+ |\mu_q |\gamma_1\rangle \langle N^*-K^*M^* | D_{0q}^1(*) \omega |N'K'M'\rangle (-1)^{N'-K^*} \]

\[ - \langle \gamma_2^+ |\mu_q |\gamma_2\rangle \langle N^*-K^*M^* | D_{0q}^1(*) \omega |N'K'M'\rangle (-1)^{N^*-K^*+N'-K'} \]

The rotation operator \( D_{0q}^1(*) \omega \) matrix elements can be evaluated (using Eqs. 3.118 and 3.125 from Zare's book) for each term.
\begin{align}
\langle N^*K^*M^*|D_{0q}^1\ast(\omega)|N'K'M'\rangle \\
= \sqrt{\frac{(2N^*-1)(2N'+1)}{8\pi}} \int D_{M^*K^*}^N \ast D_{0q}^1(\omega) D_{M'K'}^{N'} \ast d\Omega \\
= (-1)^{M'-K'-q} \sqrt{\frac{(2N^*-1)(2N'+1)}{8\pi}} \int D_{M^*K^*}^N \ast D_{0q}^1 D_{-M'K'}^{N'} d\Omega \\
= (-1)^{M'-K'-q} \sqrt{(2N^*+1)(2N'+1)} \begin{pmatrix} N^* & 1 & N' \\ -M^* & 0 & M' \\ -K^* & q & K' \end{pmatrix}
\end{align}

The non-zero dipole moment matrix elements are

\begin{align}
\langle \gamma_1^+|\mu_q|\gamma_2'\rangle &= C \sum_{l_R,\lambda_R,l_A,\lambda_A=1,-2,...} a_{l_A} (-1)^{l_A-\lambda_A} \langle l_R,\lambda_R|\mu_q |l_A,\lambda_A \rangle, \\
\langle \gamma_2^+|\mu_q|\gamma_1'\rangle &= C \sum_{l_R,\lambda_R,l_A,\lambda_A=1,-2,...} a_{l_A} (-1)^{l_R-\lambda_R} \langle l_R,-\lambda_R|\mu_q |l_A,-\lambda_A \rangle,
\end{align}

where

\begin{align}
C &= \langle \vec{X}^+|\vec{A}_{cor}\rangle \langle \nu^+_6 = 1, l^+ = 1 | \nu'^+_6 = 1, l' = 1 \rangle \\
&= \langle \vec{X}^+|\vec{A}_{cor}\rangle \langle \nu^+_6 = 1, l^+ = -1 | \nu'^+_6 = 1, l' = -1 \rangle
\end{align}

with \( \langle \vec{X}^+|\vec{A}_{cor}\rangle \) essentially unity for our model of a one-electron transition outside of a closed shell. The latter factor in \( C \), of course, represents the vibrational overlap integral. Note that the other two vibronic matrix elements in Eq. (A11) vanish because of the orthogonality of the vibrational functions. Further, we can evaluate the atomic matrix elements in Eq. (A10) to obtain

\begin{align}
\langle \gamma_1^+|\mu_q|\gamma_2'\rangle &= C \sum_{l_A,\lambda_A=1,-2,...} a_{l_A} (-1)^{l_R+l_A+q} \begin{pmatrix} l_R & 1 & l_A \\ -\lambda_R & q & \lambda_A \end{pmatrix} \langle l_R||\mu||l_A \rangle \\
\langle \gamma_2^+|\mu_q|\gamma_1'\rangle &= -C \sum_{l_A,\lambda_A=1,-2,...} a_{l_A} (-1)^{l_R+l_A} \begin{pmatrix} l_R & 1 & l_A \\ -\lambda_R & q & \lambda_A \end{pmatrix} \langle l_R||\mu||l_A \rangle
\end{align}

where \( \langle l_R||\mu||l_A \rangle \) is the reduced matrix element of the dipole moment operator.

Eqs. A9 and A12 can be combined with Eq. A8 to yield

\begin{align}
\langle \vec{X}^+, l_R\lambda_R, N^*K^*M^*|D_{0q}^1\ast \mu_q|\vec{A}E, N'K'M'\mp \rangle \\
= \mp (-1)^{M'-K'-q} \sqrt{(2N^*+1)(2N'+1)} \begin{pmatrix} N^* & 1 & N' \\ -M^* & 0 & M' \end{pmatrix}
\end{align}
where we obtain (using Equation 4.15 from Zare’s book)

\[
\begin{align*}
&\times \left\{ \langle \gamma_1^* | \mu_q | \gamma_2^* \rangle \begin{pmatrix} N^* & 1 & N' \\ -K^* & q & -K' \end{pmatrix} (-1)^{N'-K'} \\
&\quad - \langle \gamma_2^* | \mu_q | \gamma_1^* \rangle \begin{pmatrix} N^* & 1 & N' \\ K^* & q & K' \end{pmatrix} (-1)^{N^*-K^*} \right\} \\
&= \mp (-1)^{M'+N'} C \langle l_R \| \mu \| l_A \rangle \sqrt{(2N^* + 1)(2N' + 1)} \begin{pmatrix} N^* & 1 & N' \\ -M^* & 0 & M' \end{pmatrix} \\
&\times \left\{ \sum_{l_A, \lambda_A = 1, -2, ...} a_{l_A} \begin{pmatrix} l_R & 1 & l_A \\ -\lambda_R & q & \lambda_A \end{pmatrix} \begin{pmatrix} N^* & 1 & N' \\ -K^* & q & -K' \end{pmatrix} (-1)^{l_R+l_A} \\
&\quad + \sum_{l_A, \lambda_A = 1, -2, ...} a_{l_A} \begin{pmatrix} l_R & 1 & l_A \\ -\lambda_R & -q & \lambda_A \end{pmatrix} \begin{pmatrix} N^* & 1 & N' \\ -K^* & -q & -K' \end{pmatrix} (-1)^{l_R+l_A} \right\}
\end{align*}
\]

Substituting the computed matrix elements \( \langle N^* K^* M^* | D_{0q}^l(\omega) \mu_q | N' K'M' \rangle \) into Eq. A3, we obtain (using Equation 4.15 from Zare’s book)

\[
S(eN^+K^+; e'N'K'^+) = 2C^2(2N^+ + 1)(2N' + 1)
\]

\[
\times \left| \sum_{l_R, l_A, N^*, \lambda_A = 1, -2, ...} a_{n^* N^* l_R} a_{l_A} \langle l_R \| \mu \| l_A \rangle \sqrt{2N^* + 1} \begin{pmatrix} N^+ & l_A & N' \\ -K^+ & -\lambda_A & -K' \end{pmatrix} (-1)^{\lambda_R} \right|^2 
\]

\[
= 2C^2(2N^+ + 1)(2N' + 1) \sum_{l_A, \lambda_A = 1, -2, ...} \left\{ a_{l_A} \begin{pmatrix} N^+ & l_A & N' \\ -K^+ & -\lambda_A & -K' \end{pmatrix} \right\}^2 
\times \left| \sum_{n^*, l_R, N^*} a_{n^* N^* l_R} \langle l_R \| \mu \| l_A \rangle \sqrt{2N^* + 1} \begin{pmatrix} N' & N^* & 1 \\ l_R & l_A & N^+ \end{pmatrix} \right|^2 
\]

\[
= (2N^+ + 1)(2N' + 1) \sum_{l_A, \lambda_A = 1, -2, ...} a_{l_A}^2 A_{l_A} \begin{pmatrix} N^+ & l_A & N' \\ -K^+ & -\lambda_A & -K' \end{pmatrix}^2 
\]

where

\[
A_{l_A} = 2C^2 \left| \sum_{n^*, l_R, N^*} a_{n^* N^* l_R} \langle l_R \| \mu \| l_A \rangle \sqrt{2N^* + 1} \begin{pmatrix} N' & N^* & 1 \\ l_R & l_A & N^+ \end{pmatrix} \right|^2 
\]
and the quantity in curly brackets is a 6-j symbol.
TABLE I. Assignments and frequencies\textsuperscript{a} observed in the ZEKE-PFI spectra using various intermediate levels of the $\tilde{A}^2$E state of CdCH$_3$.

<table>
<thead>
<tr>
<th>Assignment Ion</th>
<th>via $\tilde{A} ,^0_0$</th>
<th>via $\tilde{A} ,^3_0$</th>
<th>via $\tilde{A} ,^6_0(K' = 2)$</th>
<th>via $\tilde{A} ,^2_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^0$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$3^1$</td>
<td>422</td>
<td>421</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$6^1 K^+ = 0$</td>
<td></td>
<td></td>
<td>739</td>
<td></td>
</tr>
<tr>
<td>$6^1 K^+ = 2$</td>
<td>747\textsuperscript{b}</td>
<td></td>
<td>758</td>
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</tr>
<tr>
<td>$6^1 K^+ = -3$</td>
<td></td>
<td></td>
<td>791</td>
<td></td>
</tr>
<tr>
<td>$3^2$</td>
<td>835</td>
<td>834</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^1$</td>
<td>1089</td>
<td></td>
<td>1089</td>
<td></td>
</tr>
<tr>
<td>$3^1 , 6^1 K^+ = 0$</td>
<td>1167\textsuperscript{b}</td>
<td></td>
<td>1154</td>
<td></td>
</tr>
<tr>
<td>$3^1 , 6^1 K^+ = 2$</td>
<td></td>
<td></td>
<td>1207</td>
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<tr>
<td>$3^3$</td>
<td></td>
<td></td>
<td>1239</td>
<td></td>
</tr>
<tr>
<td>$5^1$</td>
<td>1386\textsuperscript{b}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$6^2(a_1)$</td>
<td>1491</td>
<td></td>
<td>1492</td>
<td></td>
</tr>
<tr>
<td>$6^2(e)$</td>
<td></td>
<td></td>
<td>1534</td>
<td></td>
</tr>
<tr>
<td>$6^2(e)$</td>
<td></td>
<td></td>
<td>1568</td>
<td></td>
</tr>
<tr>
<td>$2^1 , 3^1$</td>
<td></td>
<td></td>
<td></td>
<td>1507</td>
</tr>
<tr>
<td>$2^1 , 6^1$</td>
<td></td>
<td></td>
<td></td>
<td>1846</td>
</tr>
<tr>
<td>$3^1 , 6^2(a_1)$</td>
<td>1903</td>
<td>1900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3^1 , 3^2$</td>
<td></td>
<td></td>
<td>1920</td>
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</tr>
<tr>
<td>$2^2$</td>
<td></td>
<td></td>
<td>2159</td>
<td></td>
</tr>
<tr>
<td>$2^1 , 6^2$</td>
<td></td>
<td></td>
<td>2574</td>
<td></td>
</tr>
<tr>
<td>$2^2 , 3^1$</td>
<td></td>
<td></td>
<td></td>
<td>2586</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All frequencies in cm\textsuperscript{-1}

\textsuperscript{b} Frequency is center of broad feature with no resolvable $K$ structure.
TABLE II. Molecular Parameters for $\nu_6$ level of the $\tilde{A}\,^2E_{1/2}$ state of CdCH$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Previous$^a$</th>
<th>Current$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>4.965</td>
<td>4.87</td>
</tr>
<tr>
<td>$B$</td>
<td>0.2447</td>
<td>0.2447</td>
</tr>
<tr>
<td>$a\zeta_c d$</td>
<td>632.492</td>
<td>-</td>
</tr>
<tr>
<td>$a_D\zeta_c d$</td>
<td>-0.1837</td>
<td>0</td>
</tr>
<tr>
<td>$A\zeta_t$</td>
<td>0.8626</td>
<td>-3.09</td>
</tr>
<tr>
<td>$\eta K \zeta_t$</td>
<td>-0.0101</td>
<td>-0.00981</td>
</tr>
<tr>
<td>$\epsilon_{aa}$</td>
<td>5.805</td>
<td>0</td>
</tr>
<tr>
<td>$h_1 - \epsilon_1$</td>
<td>.0286</td>
<td>0.0286</td>
</tr>
<tr>
<td>$</td>
<td>\epsilon_{2a} - h_2</td>
<td>$</td>
</tr>
</tbody>
</table>

$^a$ Values from rotational fit$^{16}$ when assigned as the origin of the $\tilde{A}\,^2E_{3/2}$.

$^b$ Values from simulation of the rotational structure of the band as the $\tilde{A}\,^2E_{1/2}$ component of the $60^1$ transition.
TABLE III. Vibrational frequencies of the $\tilde{X}$ and $\tilde{A}$ states of neutral CdCH$_3$ and its ion in its ground state

<table>
<thead>
<tr>
<th>Mode</th>
<th>CdCH$_3$ $\tilde{X}$ $^2A_1$</th>
<th>CdCH$_3$ $\tilde{A}$ $^2E$</th>
<th>CdCH$_3^+$ $\tilde{X}$ $^1A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experimental$^a$</td>
<td>calculated$^b$</td>
<td>experimental</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>2966</td>
<td>3023</td>
<td>3002</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1000</td>
<td>1003</td>
<td>1019$^c$</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>356</td>
<td>364</td>
<td>401$^c$</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>386</td>
<td>3164</td>
<td>3153</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>1389</td>
<td>1381</td>
<td>1386</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>582</td>
<td>638$^d$</td>
<td>739</td>
</tr>
</tbody>
</table>

$^a$ Robles, et al.$^{13}$

$^b$ Non-local density functional calculations$^{33}$ using the gradient functionals of Becke$^{35}$ and Perdew$^{36}$ and Volko$^{37}$ and a triple-ζ basis set on the metal atom and a triple-ζ plus polarization basis set on the C and H atoms.

$^c$Cerny, et al.$^{16}$

$^d$ Frequency obtained from rotational simulation of $\nu_6$ as described in section IV A of the text. There is evidence that Jahn-Teller and spin-orbit interactions perturb this level from its “natural” vibrational frequency.

$^e$ Frequency to position of $K=0$ stack as determined by rotational simulation of $\nu_6$. Molecular parameters for this level are $(A - B) = 5.0(1)$, $A\zeta_t = 0.4(2)$ cm$^{-1}$.
FIG. 1. The REMPI spectrum of the $\tilde{A}^2E - \tilde{X}^2A_1$ electronic transition of CdCH$_3$. The unassigned features are hot bands.
FIG. 2. The ZEKE-PFI spectra of CdCH₃ via different intermediate $\tilde{A}^2E$ vibrational levels:
(a) via the vibrationless, (b) via $\nu_3$, (c) via $\nu_6$, and (d) via $\nu_2$. 
FIG. 3. Enlarged view of CdCH$_3$ REMPI spectrum illustrating the transition to $\nu_6 = 1$ in the $\tilde{A} \ 2E$ state. The assignments are the terminal $K'$ levels with the value in parenthesis being the admixed level (see text).
FIG. 4. The ZEKE-PFI spectrum of CdCH₃ using the different $K'$ sublevels of the $\tilde{A} \, ^2E$ $\nu₆$ level (see Fig. 3) as the intermediate state.
FIG. 5. Expanded view of the ZEKE-PFI spectrum (upper) and simulations (lower) of the $K^+$ structure of $\nu_6 = 1$ in the $\tilde{X}^+ \, ^1A_1$ state of CdCH$_3^+$. Each trace is labelled by the $K' \, \tilde{A}^2E$ intermediate level of CdCH$_3$ involved in the $(1+1')$ ionization. The energy scale is with respect to the initial $\tilde{X} \, ^1A_1$ state of CdCH$_3^+$. Transitions allowed by the admixture of $d$ orbital in the $\tilde{A}$ state and governed by the $(K' + K^+ = 2)$ selection rule are off the scale of the traces with $K' = -2$ and $-3$. 
REFERENCES


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34 R. Zare, Angular Momentum (John Wiley & Sons, New York, NY, 1988).
