Photodissociation spectroscopy of stored CH\(^+\) ions: Detection, assignment, and close-coupled modeling of near-threshold Feshbach resonances

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We have measured and theoretically analyzed a photodissociation spectrum of the CH\(^+\) molecular ion in which most observed energy levels lie within the fine-structure splitting of the C\(^+\) fragment and predissociate, and where the observed irregular line shapes and dipole-forbidden transitions indicate that nonadiabatic interactions lead to multichannel dynamics. The molecules were prepared in low rotational levels \(J''=0-9\) of the vibrational ground state \(X\ ^1\Sigma^+ (v''=0)\) by storing a CH\(^+\) beam at 7.1 MeV in the heavy-ion storage ring TSR for up to 30 s, which was sufficient for the ions to rovibrationally thermalize to room temperature by spontaneous infrared emission. The internally cold molecules were irradiated with a dye laser at photon energies between 31 600–33 400 cm\(^{-1}\), and the resulting C\(^+\) fragments were counted with a particle detector. The photodissociation cross section displays the numerous Feshbach resonances between the two C\(^+\) fine-structure states predicted by theory for low rotation. The data are analyzed in two steps. First, from the overall structure of the spectrum, by identifying branches, and by a Le Roy–Bernstein analysis of level spacings we determine the dissociation energy \(D_0=(32\ 946.7\pm 1.1)\) cm\(^{-1}\) (with respect to the lower fine-structure limit) and assign the strongest features to the vibrational levels \(v'=11-14\) of the dipole-allowed \(A\ ^1\Pi\) state. The majority of the 66 observed resonances cannot be assigned in this way. Therefore, in a second step, the complete spectrum is simulated with a close-coupling model, starting from recent \textit{ab initio} Born–Oppenheimer potentials. For the long-range induction, dispersion and exchange energies, we propose an analytical expression and derive the \(C_6\) coefficients. After a systematic variation of just the vibrational defects of the four Born–Oppenheimer potentials involved, the close-coupling model yields a quantitative fit to the measured cross section in all detail, and is used to assign most of the remaining features to the dipole-forbidden \(a\ ^3\Pi\) state \((v'=17-20)\), and some to the weakly bound \(c\ ^3\Sigma^+\) state \((v'=0-2)\). The model potentials, which reproduce the spectrum and compactly represent the spectroscopic data, should help to predict more accurately C\(^+\)+H scattering in the interstellar medium. © 2002 American Institute of Physics. [DOI: 10.1063/1.1513459]

I. INTRODUCTION

Spectroscopy of diatomic molecules near the dissociation threshold allows the study of the last bound rovibrational levels in a region where the diatomic molecule may be viewed as two weakly interacting atoms. In this regime, experimental data can reveal information about the long-range interaction between the atoms as the radial wave function of a weakly bound level develops significant amplitude at large internuclear distance.\(^1\) The near-threshold levels are also intimately related to the scattering of the corresponding atoms in a slow collision. Near-threshold molecular spectroscopy can therefore provide an indirect way to measure collision properties. A more fundamental aspect is the breakdown of the Born–Oppenheimer (BO) approximation in cases where the molecule dissociates into open-shell atoms, and the resulting asymptotically degenerate BO potentials are coupled by nonadiabatic interactions.\(^2\) Examples for near-threshold systems include HD\(^+\) (Ref. 3) and, more recently, the alkali dimers (see, e.g., Ref. 4 and references therein). Here, the possibility to prepare ensembles of cold atoms has not only greatly increased the interest in atomic scattering properties,\(^4\) but also allowed new techniques like photoassociation spectroscopy,\(^5\) together with conventional molecular-beam spectroscopy,\(^6\) to explore the near-threshold region and to

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examine the breakdown of the BO approximation resulting from hyperfine interactions and applied magnetic fields.\textsuperscript{7}

In the case of the CH\textsuperscript{+} molecular ion, near-threshold dynamics have also attracted much interest, for several reasons. First, slow collisions between C\textsuperscript{+} and H occur in the interstellar medium, and the fine-structure excitation

\[ C^+(2P_{1/2}) + H(2S) \rightarrow C^+(2P_{3/2}) + H(2S) \]  

acts as a cooling mechanism if followed by a radiative relaxation of the C\textsuperscript{+} ion.\textsuperscript{8} Also, the radiative association collision

\[ C^+(2P_{1/2}) + H(2S) \rightarrow CH^+ + h\nu \]  

is a possible process for producing CH\textsuperscript{+} in cold diffuse clouds, but its rate is predicted to be much too slow to account for the observed high CH\textsuperscript{+} abundance.\textsuperscript{9} CH\textsuperscript{+} was the first molecular ion to be detected in the interstellar medium\textsuperscript{10} and plays an important role in its chemistry.\textsuperscript{11}

Second, CH\textsuperscript{+} is a model system for a special aspect of near-threshold dynamics: the influence of nonadiabatic interactions on photodissociation.\textsuperscript{12} As shown in Fig. 1, four BO potentials become degenerate at the lowest dissociation limit C\textsuperscript{+}(2P) + H(2S). The spin–orbit coupling of the C\textsuperscript{+} fragment asymptotically splits the 2P\textsubscript{1/2} and 2P\textsubscript{3/2} fine-structure states by \(\Delta E_{so} = 63.42 \text{ cm}^{-1}\).\textsuperscript{15} The spin–orbit coupling together with the mechanical rotation of the fragments about their center-of-mass leads to nonadiabatic couplings between the BO potentials.\textsuperscript{12} When predicting the photodissociation spectrum

\[ CH^+ + h\nu \rightarrow C^+(2P_{1/2,3/2}) + H(2S) \]  

from the CH\textsuperscript{+} ground state \(X^1\Sigma^+ (v''=0, J'')\) by a dipole transition to the optically allowed \(A^1\Pi\) state (see arrow in Fig. 1), Williams and Freed\textsuperscript{12} found numerous resonances corresponding to quasibound molecular levels in the energy window defined by the C\textsuperscript{+} fine-structure states. The predicted features are mainly Feshbach resonances, i.e., bound states of the closed-channel potentials correlating to the upper fine-structure limit.\textsuperscript{12} The Feshbach resonances result from nonadiabatic couplings of the \(A^1\Pi\) to the \(a^3\Pi\), \(X^1\Sigma^+\), and \(c^3\Sigma^+\) states, causing the photodissociation spectrum to become extremely complicated. The large number of predicted resonances and the irregular line shapes indicate a true multichannel regime, where the nonadiabatic couplings cannot be handled by perturbation theory. The same resonances between the C\textsuperscript{+} fine-structure levels are also important for the process of Eq. (2) since C\textsuperscript{+} ions in interstellar space mainly populate the lower 2P\textsubscript{1/2} state at temperatures of 10–100 K where collision energies are typically less than \(\Delta E_{so}\).

The interest in CH\textsuperscript{+} stimulated many detailed photodissociation experiments;\textsuperscript{16–22} all of them based on photodissociation spectroscopy. Photodissociation spectroscopy (also named “photofragment” spectroscopy) is a powerful tool for probing the internal dynamics of molecules near threshold, whereby molecules in a fast beam are photodissociated by a laser\textsuperscript{23} or a rf field,\textsuperscript{1} and the resulting fragments are detected. The benefit of using a fast molecular beam is twofold; it allows high spectral resolution because of a small Doppler broadening, and it possesses high sensitivity because of the efficient detection of the fast, directed fragments. The technique is especially suited for ionized molecules that are easily manipulated by electromagnetic fields. However, most ion sources create molecular beams with extensive internal rovibrational excitation that is often uncharacterized leading to both weak signals from individual levels and difficulties in the assignment of spectra.

Previous photodissociation studies of CH\textsuperscript{+} (Refs. 16–22) used internally hot ion beams. As a result most of these experiments focused on shape resonances (rotationally quasibound levels) of the A \(1\Pi\) state, pumped from highly excited rotational levels of the \(X^1\Sigma^+\) ground state. But the multichannel regime is predicted\textsuperscript{12} only for low rotation because the high-J shape resonances are trapped behind a rotational barrier and thus do not extend to very large internuclear distance where the nonadiabatic interactions mix different electronic states. In the isovalent SiH\textsuperscript{+} molecule with its larger fine-structure window (\(\Delta E_{so} = 287 \text{ cm}^{-1}\)), Feshbach resonances could be measured and assigned.\textsuperscript{24} Multichannel dynamics became apparent via irregularly varying linewidths, extra triplet resonances, and unexpected hyperfine splittings.\textsuperscript{24} In GeH\textsuperscript{+}, most levels of the \(A^1\Pi\) well are Feshbach resonances in the even larger window (\(\Delta E_{so} = 1767 \text{ cm}^{-1}\)) and were detected.\textsuperscript{25} For CH\textsuperscript{+}, however, the previous hot ion beam experiments produced a wealth of assigned spectroscopic structure and some unsigned structure, but no assignable Feshbach resonances.

In this paper, we present the photodissociation spectrum of internally cold CH\textsuperscript{+} ions that populate only a few rotational levels of the ground state \(X^1\Sigma^+ (v''=0)\). Internal cooling was achieved by storing the beam in a heavy-ion storage ring. The internal excitations can then decay by spontaneous emission. By this novel type of photodissociation spectroscopy, the near-threshold Feshbach resonances are accessible for the first time. We have already presented a brief account of the results,\textsuperscript{26} with emphasis on the observation.
that the rovibrational distribution of the ions reaches room temperature.

In the present article, we provide the full analysis of the data. The near-threshold Feshbach resonances turn out to be of a tremendous spectroscopic value. They allow us to extract a much more precise value for the dissociation energy. The strongest features in the spectrum mark the last vibrational levels of the A $^1$II potential and reveal its vibrational defect. Furthermore, dipole-forbidden transitions to the last vibrational levels of the $a^3$II state and even of the weakly bound $c^3$Σ $^+$ state (Fig. 1) are observed. This directly shows the effect of the nonadiabatic interactions and allows us to extract the vibrational defects of the $a$ $^3$II and $c$ $^3$Σ $^+$ potentials, too. Transitions to $X$ $^1$Σ $^+$ levels are not observed, but the intensities and shapes of other resonances are sufficient to determine the vibrational defect of the $X$ $^1$Σ $^+$ state indirectly. Finally, the new data are relevant for future, more precise calculations of processes (1) and (2).

Among our results, only the overall structure of the experimental spectrum, the dissociation energy, and most A $^1$II features could be handled by a conventional spectroscopic analysis, with the majority of the observed features left unassigned. The complete analysis required a large joint theoretical effort. The use of extensive close-coupling model calculations, based on those described in Ref. 12, allowed the theoretical effort. The use of extensive close-coupling model calculations, based on those described in Ref. 12, allowed the extraction of the vibrational defects of the A $^1$II and $c$ $^3$Σ $^+$ potentials, too. Transitions to $X$ $^1$Σ $^+$ levels are not observed, but the intensities and shapes of other resonances are sufficient to determine the vibrational defect of the $X$ $^1$Σ $^+$ state indirectly. Finally, the new data are relevant for future, more precise calculations of processes (1) and (2).

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The following section provides the essential aspects of the theory needed to understand the analysis of our results, and briefly reviews previous calculations and measurements. Our experiment is described in Sec. III. Section IV starts with the standard spectroscopic analysis of the data, and this is followed by the full analysis based on the close-coupling simulations, in order to show what additional information can be extracted using this more sophisticated analysis. The paper ends with a conclusion (Sec. V).

II. THEORY AND PREVIOUS WORK

A. Theory: Nonadiabatic couplings in CH$^+$

In this section, we briefly discuss the nuclear dynamics near the lowest dissociation limit of CH$^+$, following Ref. 12. We start from the Hamiltonian, define the relevant molecular states in Hund’s case (a) basis set and derive the potential matrix. This matrix serves to identify and discuss the nonadiabatic couplings, to calculate adiabatic potentials, and will be an important tool for the analysis of the experimental data.

The Hamiltonian for the motion of the electrons and nuclei in the center-of-mass system of the molecule is a sum of three terms,

$$H(r) = H_{\text{elec}}(r) + T_{\text{muc}}(r) + H_{\text{so}}(r),$$

(4)

where $r$ is the relative position of the nuclei, $H_{\text{elec}}(r)$ is the Born–Oppenheimer Hamiltonian for the interactions between the electrons and the nuclei within the body-fixed coordinate system, $T_{\text{muc}}(r)$ is the nuclear kinetic energy operator, and $H_{\text{so}}(r)$ is the spin–orbit operator. Spin–spin, hyperfine, spin–rotational, and other interactions are not included in $H$ because they are much smaller than the spin–orbit and rotational contributions.

As usual, the nuclear kinetic energy is split into a radial and a rotational part,

$$T_{\text{muc}}(r) = T_{\text{rad}}(r) + T_{\text{rot}}(r)$$

(5)

$$= -\frac{\hbar^2}{2\mu r} \frac{\partial^2}{\partial r^2} r + \frac{\mathbf{I}^2}{2\mu r^2},$$

(6)

where $\mu$ is the reduced mass calculated from the atomic masses of the fragments, and $\mathbf{I}$ is the angular momentum associated with the rotation of the fragments about the center-of-mass.

Consider an electronic-rotational basis set $|JM\alpha\rangle$ which spans the space of electronic and rotational motion of the molecule. Since $H$ commutes with the total angular momentum $\mathbf{J}$, $J$ and $M$ are good quantum numbers, $M$ being the projection of $\mathbf{J}$ on the space-fixed $z$ axis. A general electronic-rotational basis can thus be labeled $|JM\alpha\rangle$, where $\alpha$ collectively designates some set of additional quantum numbers required to specify the states uniquely. An electronic-rotational basis transforms the molecular Schrödinger equation into a set of coupled radial equations for the nuclear wave functions, with the $r$-dependent potential matrix,

$$W_{JM\alpha,J'M'\alpha'}(r) = \langle JM\alpha | [H_{\text{elec}}(r) + T_{\text{rad}}(r) + H_{\text{so}}(r)] | J'M'\alpha' \rangle,$$

(7)

which we now derive.

As a particular electronic-rotational basis for the representation of the potential matrix, we chose the Hund’s case (a) or “molecular” basis set

$$|JM\alpha\rangle = |JM\Lambda S\Sigma\tilde{p}\rangle.$$

(8)

Apart from total angular momentum $(J, M)$, this basis is defined by the projection $\Lambda$ of the electronic orbital angular momentum $\mathbf{L}$ onto the internuclear axis and by the total electronic spin $S$ and its projection $\Sigma$ onto the internuclear axis. $\Lambda$ is assumed non-negative because the states are defined as symmetrized linear combinations of the body-fixed molecular electronic basis functions $|\Lambda S\Sigma\rangle$ and $|\Lambda S\Sigma^\dagger\rangle$ to make them eigenstates of the space-fixed inversion operator with eigenvalue $(-1)^{J+\tilde{p}}$. As usual, electronic-rotational states with $\tilde{p} = 0$ and $\tilde{p} = 1$ are called $e$ and $f$ states, respectively. Since $H$ commutes with this inversion operator, the matrix $W(r)$ cannot couple $e$ to $f$ states. Both groups can thus be viewed as separate parity blocks.

For the four electronic states correlating to the C$^+$ $(2^2P)$ + H$(2S)$ dissociation limit, there are 12 electronic-rotational states for given $J$ and $M$, six per parity block,
TABLE I. Potential matrix for CH⁺ in the molecular basis. BO potentials are denoted by \( U_{\lambda,\sigma}(r) \). Spin–orbit interactions contain \( A = \Delta E_{J}/3 = 21.14 \text{ cm}^{-1} \), and rotational interactions contain \( B(r) = h^{2} / (2\mu r^{2}) \). \( x \) denotes \( J(J+1) \). Only the lower half of the symmetric matrix is provided. For the \( e(f) \) matrix, include \( e(f) \) states and read upper (lower) signs.

| \( |\Pi_{1}^{x} \rangle \) | \( |\Pi_{1}^{y} \rangle \) | \( |\Pi_{0}^{x} \rangle \) | \( |\Pi_{0}^{y} \rangle \) | \( |\Sigma_{0}^{+} \rangle \) | \( |\Sigma_{0}^{-} \rangle \) |
|---|---|---|---|---|---|
| \( \langle \Pi_{1}^{x} | \Pi_{1}^{x} \rangle \) | \( \langle \Pi_{1}^{y} | \Pi_{1}^{y} \rangle \) | \( \langle \Pi_{0}^{x} | \Pi_{0}^{x} \rangle \) | \( \langle \Pi_{0}^{y} | \Pi_{0}^{y} \rangle \) | \( \langle \Sigma_{0}^{+} | \Sigma_{0}^{+} \rangle \) | \( \langle \Sigma_{0}^{-} | \Sigma_{0}^{-} \rangle \) |
| \( U_{1,1} + 3A + B(x+2) \) | \( -B \sqrt{2} \) & \( -B \sqrt{2} \) | \( U_{1,1} + 2A + B(x+2) \) | \( U_{1,1} + A + B(x+2) \) | \( U_{1,1} + 2A + B(x+2) \) |
| \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) |
| \( \langle \Pi_{1}^{y} | \Pi_{1}^{y} \rangle \) | \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) |
| \( \langle \Sigma_{0}^{+} | \Sigma_{0}^{+} \rangle \) | \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) & \( \ldots \) |

representation in the molecular basis. Note that this procedure amounts to approximating these matrix elements at all internuclear distances by their asymptotic values.12 This is a reasonable assumption, since \( T_{\text{rot}}(r) \) and \( H_{\text{so}}(r) \) will become more important at large internuclear separation as \( H_{\text{elec}}(r) \) \( \to 0 \). Adding the resulting case (a) matrices for \( T_{\text{rot}}(r) \) and \( H_{\text{so}}(r) \) to the BO potentials finally yields the potential matrix of Table I.30

Inspection of the table reveals spin–orbit coupling between \( |\Pi_{1}^{x} \rangle \), \( |\Pi_{1}^{y} \rangle \), and \( |\Sigma_{1}^{+} \rangle \), and also between \( |\Pi_{0}^{x} \rangle \) and \( |\Sigma_{0}^{+} \rangle \) or \( |\Sigma_{0}^{-} \rangle \) for \( e(f) \), respectively. Rotational coupling appears between those triplet states whose \( \Omega \) quantum numbers differ by one or zero, and between the \( |\Pi_{1}^{x} \rangle \) and \( |\Sigma_{0}^{+} \rangle \) states in the \( e \) parity block. By “rotational coupling” we summarize all off-diagonal matrix elements of the operator \( T_{\text{rot}}(r) \), whether they be rotational-electronic (arising from the \( J \cdot L \) or \( J \cdot S \) terms) or spin-electronic (from \( L \cdot S \)). As the spin–orbit splitting of the \( C^+ \) ion is moderate and the reduced mass of \( CH^+ \) is small, spin–orbit coupling and rotational coupling are of similar magnitude.

Figure 2 shows the adiabatic potentials obtained by diagonalization of the potential matrix on a grid of \( r \) values. The underlying long-range BO potentials \( U_{\lambda,\sigma}(r) \) were assumed to have the shape computed by Harel and Baez.31,32 Note that the new electronic-rotational eigenstates that follow from the diagonalization are not pure case (a) states anymore, but \( r \)-dependent mixtures. The case (a) labeling of the adiabatic potentials in Fig. 2 only indicates to which state the curves correlate at small \( r \). All curves that correlate to the upper \( C^+ \) fine-structure state can support bound states, the highest of which lie above the lower \( C^+ \) fine-structure limit and can therefore predissociate via nonadiabatic couplings to the continuum of states correlating to the lower asymptote. Note that in this adiabatic picture, the coupling does not arise from the spin–orbit and rotational operators, but from the radial part of the nuclear kinetic energy in Eq. (6) that acts on the \( r \)-dependent basis set.31

B. Previous calculations of photodissociation resonances

Energies and predissociation dynamics of quasibound states in \( CH^+ \) have been calculated in a number of papers. Note on the \( ab \ initio \) BO potentials of Green et al.,13 Abovoll et al.,34 and Uzer and Dalgalno35 predicted shape resonances of the \( A \) \( 1\Pi \) potential, as well as the probability for
tunneling through the rotational barrier. Since nonadiabatic effects arising from the other curves have almost no effect on the shape resonances, such couplings were not included.

When Graff et al. calculated the energies and widths of the $A$ 1$\Pi$ resonances, they included the $A$ 1$\Pi$ quasibound levels between the $C^+$ fine-structure levels. Since the $A$ 1$\Pi$ channel is closed below the $C^+$($2P_{3/2}$) limit, these quasibound levels are not shape but Feshbach resonances and cannot decay by tunneling through the centrifugal barrier, but only by nonadiabatic coupling to the curves correlating to the lower fine-structure limit. To account for this, Graff and coworkers used a perturbation approach. They first diagonalized the $\Omega=1$ submatrix of Table I including the BO and spin–orbit matrix elements to obtain adiabatic potentials in which to compute energy levels, along with a new $r$-dependent electronic-rotational basis. From the known $r$-dependence, they calculated the radial coupling matrix element between the adiabatic $A$ 1$\Pi$ and $a$ 3$\Pi_1$ states and found the strongest influence around 3 Å. The radial predissociation width was then calculated from the integral over the corresponding bound and continuum radial wave functions. The probability for predissociation via rotational coupling to the $X$ 1$\Sigma^+$ curve was estimated analogously by means of the corresponding matrix element (Table I). Several vibrational states of the $A$ 1$\Pi$ curve were found, most with predissociation widths of a few cm$^{-1}$ or more.

The photodissociation spectrum of CH$^+$ starting from the lowest rotational levels of the ground vibrational state of $X$ 1$\Sigma^+$ was subsequently predicted by Graff and Moseley,

based on the $A$ 1$\Pi$ resonance energies and widths in Ref. 36. From a single rotational state $J''$ at an energy $E_{J''}$ above the ground state $X$ 1$\Sigma^+ (v''=0, J''=0)$ the Feshbach resonances between the fine-structure limits can only be reached by photon energies $\tilde{\nu}$ in the energy window,

$$D_0 - E_{J''} \leq \tilde{\nu} \leq D_0 - E_{J''} + \Delta E_{\text{so}},$$

where $D_0$ is the dissociation energy, referred to the lower limit. For lower photon energies no photodissociation occurs, for higher energies only nonresonant dissociation to the continuum of the $A$ 1$\Pi$ state is possible when we exclude shape resonances. Theory therefore expects a single initial rotational state $J''$ to contribute to Feshbach resonances in the window defined by Eq. (14), and a continuous spectrum at higher energies. Besides photodissociation, the $A$ 1$\Pi$ resonances from Ref. 36 also served to calculate the rate coefficient for radiative association [Eq. (2)].

Williams and Freed tackled the problem using the full quantum theory of diatomic photodissociation developed by Singer et al. In order to include nonadiabatic coupling, the radial Schrödinger equations, coupled by the potential matrix of Eq. (7), were solved by a close-coupling code for the multichannel continuum wave functions under the appropriate scattering boundary conditions. The cross section for photodissociation from the ground state $X$ 1$\Sigma^+ (v''=0, J'')$ was obtained from the multichannel continuum wave function by calculating the transition dipole moment matrix element between the $A$ 1$\Pi$ component of the multichannel wave function and the $X$ 1$\Sigma^+$ radial wave function.

The fully coupled treatment predicts novel effects in the photodissociation spectrum, the most striking being the appearance of multichannel resonances, i.e., quasibound states residing on an electronic surface other than the dipole allowed $A$ 1$\Pi$ surface. In fact, all adiabatic curves of Fig. 2 are found to contribute features to the spectrum, essentially eliminating all electronic selection rules (including spin). The multichannel resonances are mainly of Feshbach type, but some non-$A$ 1$\Pi$ shape resonances are predicted as well, especially for the curves correlating to the lower limit. In contrast to the simple Lorentzian line shapes from the perturbation treatment, the close-coupling calculation predicts irregular, non-Lorentzian line shapes due to interference between the closely spaced resonances, making the model spectrum very sensitive to the underlying BO potentials.

C. Previous photodissociation spectroscopy of CH$^+$

Photodissociation spectroscopy on CH$^+$ was first performed by Carrington and Sarre and by Cosby et al. Both used fast beams of CH$^+$ ions from electron-impact ion sources and Doppler-tuned them into resonance with lines of argon- and krypton-ion lasers. The photodissociation rate and the kinetic energy release were measured by energy-analyzing and counting the $C^+$ fragments. Although the Doppler-tuning range was restricted to only a few cm$^{-1}$ per laser line, Cosby et al. reported 37 unassigned transitions around 28 000 cm$^{-1}$ with energy releases of less than 350 cm$^{-1}$, and were the first to invoke nonadiabatic resonances between the $C^+$ fine structure limits as a possible explanation for the high density of levels.
The first CH\textsuperscript{+} photodissociation spectrum to be successfully assigned was measured by Helm et al.\textsuperscript{18} who used tunable dye lasers to scan a large frequency region between 16 000 and 19 600 cm\textsuperscript{-1}. They identified 32 quasibound rotational levels of the A 1\Pi potential with rotational quantum numbers 12 \leq J' \leq 35 and vibrational quantum numbers 0 \leq v' \leq 10 resulting from A 1\Pi – X 1\Sigma\textsuperscript{+} transitions. Helm et al. determined a new set of spectroscopic constants for both the X 1\Sigma\textsuperscript{+} and the A 1\Pi potential, then derived from the measured fragment kinetic energy release a better value for the dissociation energy \( D_0 = 32.907(23) \) cm\textsuperscript{-1}, and condensed this information into BO potentials consistent with their data. It is essentially these potentials on which Graff et al. based their calculations.\textsuperscript{12,36} Apart from the assigned A 1\Pi – X 1\Sigma\textsuperscript{+} transitions, a bandlike region of very high line density around 19 000 cm\textsuperscript{-1} was also observed, similar to Cosby’s spectrum\textsuperscript{17} around 28 000 cm\textsuperscript{-1}. In addition, isolated resonances in the UV range were detected and attributed to transitions from the long-lived a 1\Pi state to \( B + \) 3\Sigma\textsuperscript{-} levels that then predissociated (Fig. 1).

The experimental data on the A 1\Pi shape resonances were refined by Sarre et al.\textsuperscript{19} who remeasured many of the transitions reported by Helm\textsuperscript{18} at high resolution (0.003 cm\textsuperscript{-1}) to obtain more accurate line positions and widths. These results were later compared to a perturbation calculation\textsuperscript{38} similar to Graff’s.\textsuperscript{36} Application of the close-coupling theory to compute the widths of the shape resonances yielded good agreement and allowed the BO potentials to be further improved.\textsuperscript{39} When performing a high-resolution study of the isotopomer \(^{13}\text{CH}\textsuperscript{+}\), Whitham et al. found the A 1\Pi (\( v' = 5,J' = 24 \)) shape resonance to be hyperfine-split.\textsuperscript{22} The hyperfine splitting, which unambiguously indicates some triplet admixture in the singlet wave function,\textsuperscript{22} makes this resonance the first feature with definite multichannel character assigned in CH\textsuperscript{+}. But the more drastic multichannel effects predicted for the near-threshold Feshbach resonances could not be tested.

Cosby’s suggestion\textsuperscript{17} that the bandlike dense spectra\textsuperscript{17,18} might actually consist of such multichannel resonances was disapproved by Sarre and Whitham,\textsuperscript{20} who showed that these structures rather arose from bound-bound-free transitions from bound levels near the C\textsuperscript{+} + H dissociation limit to long-range states at the higher C(3P) + H\textsuperscript{+} or C(1D) + H\textsuperscript{+} asymptote, and back to free states just above the C\textsuperscript{+} + H asymptote.

Carrington and Softley\textsuperscript{21} made an attempt to study the near-threshold resonances by recording an infrared photodissociation spectrum of CH\textsuperscript{+} between 900 and 1100 cm\textsuperscript{-1}. They detected 87 transitions. But even with the help of a detailed model spectrum, computed by calculating quasi-bound levels in the adiabatic potentials obtained by diagonalizing the full potential matrix (Table I), only a few transitions could be tentatively assigned. The difficulties were due to the uncertainties in the potentials, to the use of a single-channel adiabatic model, and to the lack of knowledge of the initial rovibrational states.

In summary, all previous experiments failed to detect and assign resonances between the C\textsuperscript{+} fine-structure limits.
the ion beam was a few cm and its position in the interaction region (Fig. 3) was determined using beam scrapers.

A. Laser system

The experiment used a XeCl excimer laser to pump a tunable dye laser, operated with Rhodamine 101 dye between 616 and 660 nm to generate red pulses (length ~15 ns, energy ~20 mJ). The linewidth of the laser was about 0.3 cm⁻¹. The wavelength of the laser was calibrated optogranically to a single Ne atomic absorption line. The relative accuracy during scanning was limited to ±0.4 cm⁻¹ by the nonlinearity of the dye laser tuning mechanism. The red pulses were frequency-doubled in a BBO crystal to produce UV pulses with an energy of 2–4 mJ and an estimated linewidth of 0.5 cm⁻¹. This width roughly defined the total experimental resolution since the Doppler broadening due to the ion velocity spread was only 0.1–0.2 cm⁻¹. The linearly polarized UV laser beam was adjusted to the known position of the ion beam in the 10 m long straight section of the ring (Fig. 3) using dielectric mirrors and a telescope. The laser beam diameter was 2–4 mm, i.e., much smaller than the cross section of the ion beam. The energy of the pulses was measured with photodiodes that were calibrated against a background count rate of around 10⁵ s⁻¹. The strong narrow peak arises from scattered UV light, while the background is shown as inset of Fig. 3. Before the laser pulse, corresponding to the maximum flight time through the interaction region (10 m), while the background fragments arrive steadily. We therefore measured the arrival times of the fragments shortly before and after the laser pulse using a time-to-digital-converter. A corresponding time-of-flight histogram is shown as inset of Fig. 3. Before the laser pulse and later than 1.2 μs after the pulse, only a constant background of collision-induced fragments caused by the residual gas can be seen (events before the triggering laser pulse appear because the detector pulses were electronically delayed). The strong narrow peak arises from scattered UV photons detected on the MCP. The broad peak between 0.1 and 1.1 μs contains the photofragments. The shape of this photopake reflects the transverse density of the ion beam as it is focused by quadrupole magnets between the dipole magnets. The histogram in Fig. 3 contains the summed fragments from a large number of laser pulses. The maximum number of detected photofragments from a single laser pulse was limited by the deadtime of the MCP detector and the pulse-shaping electronics (130 ns). In our experiment, the ion current and laser intensity typically lead to less than five fragments per pulse. Pulse pile-up was taken into account in the evaluation of the spectra (Sec. III C), but the correction was small except for some strong photodissociation resonances from the b ³Σ⁺→a ³Π system. The exact intensity of these features, however, is unimportant for the present work (see Sec. IV A).

Besides the collision-induced background, a second background contribution must be considered. The dipole magnet which separated the C⁺ fragments from the CH⁺ beam had a magnetic flux density of B=1.2 T which amounted to a motional electric field of ~120 kV/cm in the rest frame of the ions, enough to allow field-dissociation of CH⁺ molecules in weakly bound states. If such states were populated by the laser pulse and then field-dissociated in the magnet, the corresponding fragments were counted as photodissociation fragments.

We measured the photodissociation cross section for a single photon wavelength as follows: The data acquisition system included the dye laser to the required frequency and triggered the injection of ions into the ring. The laser ran at a repetition rate of 200 Hz. At each pulse, the data acquisition system measured and stored (1) the arrival time of all fragments within a few μs around the laser pulse, (2) the laser pulse energy seen by the photodiode, (3) the average background rate of C⁺ fragments since the previous laser pulse, and (4) the storage time for which the ions had been stored in the ring, i.e., the time since injection. After 20–30 s storage time, the laser wave number was incremented by 0.25 or 0.5 cm⁻¹, and this procedure was repeated. The interval measured in a typical scan (1–2 h) was ~100 cm⁻¹. To cover the whole region of interest (31 600–33 400 cm⁻¹) required many such scans. The photon wave number v in the rest frame of the molecules was calculated from the wave number of the laser and was Doppler-corrected for the velocity of the molecules as determined from the Schottky spectrum.

B. Detection scheme

All C⁺ fragments produced in the interaction region were mass-separated from the CH⁺ beam in the first downstream dipole magnet and detected on a microchannel plate detector (MCP) (Fig. 3). Even without the laser, there was a C⁺ background count rate of around 10⁵ s⁻¹ due to dissociation of CH⁺ ions upon collisions with residual gas. The laser-induced C⁺ fragments were distinguished from this background because they only occurred within 1 μs after the laser pulse, corresponding to the maximum flight time through the interaction region (10 m), while the background fragments arrive steadily. We therefore measured the arrival times of the fragments shortly before and after the laser pulse using a time-to-digital-converter. A corresponding time-of-flight histogram is shown as inset of Fig. 3. Before the laser pulse and later than 1.2 μs after the pulse, only a constant background of collision-induced fragments caused by the residual gas can be seen (events before the triggering laser pulse appear because the detector pulses were electronically delayed). The strong narrow peak arises from scattered UV photons detected on the MCP. The broad peak between 0.1 and 1.1 μs contains the photofragments. The shape of this photopake reflects the transverse density of the ion beam as it is focused by quadrupole magnets between the dipole magnets. The histogram in Fig. 3 contains the summed fragments from a large number of laser pulses. The maximum number of detected photofragments from a single laser pulse was limited by the deadtime of the MCP detector and the pulse-shaping electronics (130 ns). In our experiment, the ion current and laser intensity typically lead to less than five fragments per pulse. Pulse pile-up was taken into account in the evaluation of the spectra (Sec. III C), but the correction was small except for some strong photodissociation resonances from the b ³Σ⁺→a ³Π system. The exact intensity of these features, however, is unimportant for the present work (see Sec. IV A).

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C. Evaluation of spectra

The average total number N of photofragments measured at a wave number v is given by

\[ N = \chi \Phi \sigma(v) \],

(15)

where \( \sigma(v) \) is the photodissociation cross section, \( \chi \) is the column density of irradiated ions, and \( \Phi \) is the number of photons. Equation (15) holds in particular for the \( N_{ji} \) photofragments produced by a single laser pulse \( i \) during the scan \( j \), with \( \Phi_{ji} \) photons and a momentary ion column density \( \chi_{ji} \). Thus, the cross section at wave number v is given by

\[ \sigma(v) = \frac{\sum_{ji} N_{ji}}{\sum_{ji} \chi_{ji} \Phi_{ji}} \],

(16)

where we have summed over all laser pulses at the wave number v. Note that the pulses at this wave number can originate from more than one scan because scan intervals generally overlapped. In order to get spectra for different ion storage times, the summation in Eq. (16) was further restricted to data coming from certain storage time windows, for example, 7 s < t_i < 10 s.

The quantities on the right-hand side of Eq. (16) were determined from the raw data as follows. The number of
photofragments $\sum_{ji} N_{ji}$ was determined by filling the fragment arrival times of all relevant laser pulses into a histogram as in Fig. 3, and summing over the photopake (disregarding the events from scattered light). The resulting number was corrected for detector deadtime effects, which depended on the average rate in the photopake, and then for the background count rate.

The irradiated column density $\chi_{ji}$ of ions was assumed proportional to the momentary ion current $I_{ji}$,

$$\chi_{ji} = \xi_j I_{ji}, \quad (17)$$

where $\xi_j$ is an unknown geometrical overlap factor that can differ between scans if the ion beam drifted or the laser beam was readjusted. An absolute current measurement was impossible at TSR for the weak ion beam considered here. Therefore, the ion current was assumed to be proportional to $u_{ji}$, the average $C^+$ background rate since the previous laser pulse,

$$I_{ji} = q_j u_{ji}. \quad (18)$$

As the unknown proportionality factor $q_j$ depended on the residual gas density in the interaction region, it can also vary between scans. Finally, the number of photons $\Phi_{ji}$ was directly determined from the calibrated photodiode signal of the laser pulse.

Substituting into Eq. (15), the cross section is

$$\sigma(\nu) = \frac{\sum_{ji} N_{ji}}{\sum_{ji} \xi_j q_j u_{ji} \Phi_{ji}} \frac{\sum_{ji} \xi_j q_j u_{ji} \Phi_{ji}}{\sum_{ji} q_j u_{ji} \Phi_{ji}}, \quad (19)$$

where the unknown factors have been absorbed into a single factor $q_j = \xi_j q_j$ that may vary from one scan to the next. As these factors could not be determined absolutely, the current experiment only provides a relative measurement of the cross section.

The data from several scans were to be merged into a single spectrum according to Eq. (19). As a result the relative $q_j$ values had to be known in order to avoid artificial steps in the spectrum. Such cross-normalization was especially important here because the spectrum turned out to have many broad and steplike features (see below).

The relative determination of the $q_j$ was achieved as follows: First, equal factors $q_j = 1$ were assumed for all scans, and the cross section was calculated for all scans separately according to Eq. (19). Whenever two scans $j$ and $k$ shared common wave number points in the same storage time window, the average ratio of their respective cross section values was determined by linear regression and used as a measure for $q_j/q_j$. By finding these ratios for all possible pairs of overlapping scans and arbitrarily defining one scan to have $q = 1$, the factors were finally computed for all scans. To interlock as many scans as possible, we performed extra scans with lower resolution but with wider spectral range.

Merging data from overlapping scans also required to evaluate Eq. (19) not for single wave numbers, but for small wave number intervals. That is, data with negligible wave number differences were added to the same wave number bin, in order to improve counting statistics. The bin size was 0.25 cm$^{-1}$, which is tolerable given the experimental resolution of 0.5 cm$^{-1}$.

**D. Uncertainties**

The total combined uncertainty of the energy scale in the ion rest frame was estimated from the uncertainties of the relevant input data. The energy in the lab frame had a standard uncertainty of 0.4 cm$^{-1}$ (after frequency doubling) arising from the mechanical nonlinearity of the dye laser drive. The Doppler correction was affected by the relative uncertainty of the ion revolution frequency ($1.1 \times 10^{-4}$), and by the uncertainty of the actual circumference of the ion orbit in the TSR (5 cm). Finally assigning the true measured wave numbers to bins of width 0.25 cm$^{-1}$ introduced an additional uncertainty of 0.07 cm$^{-1}$ (assuming a uniform probability distribution over the bin). Combining all components yields a combined standard uncertainty of 1.1 cm$^{-1}$ in the energy scale.

The combined standard uncertainty of the cross section was calculated for each wave number point according to the measured quantities entering Eq. (19). It was usually dominated by photofragment counting statistics. Since data of different quality was mixed in Eq. (19), adjacent points could have quite different error bars, which in some cases obscured the spectrum. In regions of small stepwidth (0.25 cm$^{-1}$) the spectra were thus smoothed by replacing the cross section at wave number $\nu_k$ by the uncertainty-weighted average,

$$\overline{\sigma}(\nu_k) = \frac{\sum a_i \sigma(\nu_{k+i})}{\sum |a_i|}, \quad (20)$$

$$a_i = \frac{b_i}{(\Delta \sigma)^2(\nu_{k+i})}, \quad (21)$$

over the point and its two nearest neighbors $\nu_{k-1}$ and $\nu_{k+1}$, with coefficients $b_0 = 0.5$ and $b_{\pm 1} = 0.25$. Given the low experimental resolution (0.5 cm$^{-1}$), this procedure does not lead to significant additional line broadening. Smoothed spectra are explicitly marked in the following.

**IV. RESULTS AND DISCUSSION**

**A. Overview of spectrum**

Figure 4 displays the measured photodissociation cross section for CH$^+$ as a function of the photon wave number. The features can be divided into two groups: First there is a band of very strong (many are off-scale) narrow resonances to the red of 32 400 cm$^{-1}$ shown in gray. Second, we see in Fig. 4 a continuous spectrum in black whose background increases as one moves to the blue from 31 700 cm$^{-1}$ and on which there are superimposed small resonances (black).

The photodissociation spectrum changes dramatically with increasing storage time of the ions in the ring (see also Ref. 26). The dominance of the very strong narrow band decreases in intensity with time, with the features furthest from the band head decreasing most rapidly, i.e., the remaining features are dominated by the bandhead. The relative intensity of the continuous spectrum is seen to increase and to shift toward the maximum around 33 000 cm$^{-1}$. Figure 4 displays the data in three portions, each of which is shown at the storage time where the continuous spectrum appeared most pronounced. For example, the spectral features in the
region above 32 500 cm\(^{-1}\) are strongest for \(t_s=15\text{–}30\text{ s.}\) In contrast, no resonances are seen here for short storages times \(t_s<1\text{ s.}\)\(^{26}\)

The strong band of narrow resonances coincides with the 2–0 band of the \(b\,^3\Sigma^+\rightarrow a\,^3\Pi\) system observed previously at low resolution.\(^{41,42}\) This means that \(\text{CH}^+\) molecules in the metastable \(a\,^3\Pi\) \((v''=0)\) state are present in the ion beam. These molecules are then excited to bound levels of the \(b\,^3\Sigma^+\) curve where they are predissociated by the repulsive \(c\,^3\Sigma^+\) curve (Fig. 1). This is consistent with an earlier experiment, in which dissociative recombination of \(\text{CH}^+\) was studied at the TSR storage ring\(^{33}\) with the same ion beam settings as in the present experiment, in particular with the same ion source. In this earlier measurement, we found \(7(1)\) s for the radiative lifetime of the \(a\,^3\Pi\) state. At injection, \(60\%\text{-}70\%\) of the \(\text{CH}^+\) ions were in the \(a\,^3\Pi\) state, with the rest of the molecules being in the \(X\,^1\Sigma^+\) ground electronic state. This same data showed vibrational cooling within the \(a\,^3\Pi\) state.\(^{33}\) The intensity shift toward the band head, which is seen here, is due to rotational cooling within \(a\,^3\Pi\) \((v''=0)\).\(^{26}\)

In addition to the 2–0 band, the 3–0 band and some high rotational lines of the 4–0 band are present in the photodissociation spectrum at higher energies not shown here.\(^{26}\) We have performed a rotational assignment and analysis of the \(b\,^3\Sigma^+\rightarrow a\,^3\Pi\) bands in order to safely discern the lines from the rest of the spectrum. The assigned \(b\,^3\Sigma^+\rightarrow a\,^3\Pi\) resonances will be shown in gray in all figures and will not be discussed further.

The stored \(\text{CH}^+\) molecules in the electronic ground state \(X\,^1\Sigma^+\) are known from the dissociative recombination experiment\(^{33}\) to cool vibrationally to \(v''=0\) within 2–3 s. The continuous spectrum with the superimposed resonances (black in Fig. 4) must thus be due to photodissociation from \(X\,^1\Sigma^+\) \((v''=0)\) (depicted by the arrow in Fig. 1). The resonances turn out to be clustered in groups of width \(\Delta E_{so}\) separated by flat regions, the height of the underlying continuum increasing after each group. This qualitatively matches the spectrum expected for photodissociation from the lowest rotational states, each of which contributes resonances in the energy window defined by Eq. (14), and a continuum at higher energies. The separation between the resonance groups becomes less clear at the high energy region of the spectrum where the rotational separation between adjacent clusters becomes smaller than \(\Delta E_{so}\).

### B. Assignment of initial states: Preliminary dissociation energy

The assignment of the resonance groups to the initial states \(X\,^1\Sigma^+\) \((v''=0,J'')\) is easy because the relative energies of these states (Table II) are accurately known from emission spectroscopy.\(^{44}\) By varying the dissociation energy \(D_0\), and requiring that all resonances lie within at least one of the \(J''\)-windows defined by Eq. (14), we find the assignment of initial \(J''\) states indicated in Fig. 4. The spectrum contains

![Image](https://jcp.aip.org/jcp/figures/fig4.pdf)

**FIG. 4.** Overview of measured spectrum, consisting of the \(b\,^3\Sigma^+\rightarrow a\,^3\Pi\) 2–0 band (gray) and a continuous spectrum superimposed with weaker resonances (black), due to photodissociation from \(X\,^1\Sigma^+\) \((v''=0,J'')\). The \(X\,^1\Sigma^+\) spectrum resembles a stairway. Each step consists of a resonance group and a continuous spectrum extending to the blue. The steps can be assigned to initial rotational levels \(J''\) with help of Eq. (14). The spectrum is shown in three portions. For each portion, the storage time interval was chosen such that the \(X\,^1\Sigma^+\) contribution appeared most pronounced.
FIG. 5. Resonance group assigned to \(J^*=5\). Lower and upper threshold according to Eq. (14) are indicated by dashed lines, assuming \(D_0 = 32,948\) cm\(^{-1}\). The continuous background from \(J^* > 5\) (solid line) was estimated by a linear extrapolation from the flat spectrum below the lower limit.

contributions \(J^* = 0, \ldots, 9\). The groups belonging to \(J^* = 6, \ldots, 9\) are superimposed with the triplet band. In contrast to the signal from \(J^* = 0, \ldots, 5\), they appear strongest at short storage time (see Fig. 4). This is due to rotational cooling within \(X^1 \Sigma^+ (v'' = 0)\), which was quantitatively studied in Ref. 26. The rotational distribution was shown to reach thermal equilibrium with the room temperature Planck radiation in the beam tube of the storage ring.

When varying \(D_0\) to fit all resonances simultaneously into the \(J^*\)-windows defined by Eq. (14), we find that this condition could only be met when we assumed the windows to be slightly wider than \(\Delta E_{\text{so}}\). This indicates bound states above or below the fine-structure window in Fig. 2. While levels above the \(+2P_{3/2}\) dissociation limit can be readily explained\(^{12}\) by shape resonances of any of the potentials correlating to the upper limit in Fig. 2, bound states below the lower fine-structure limit cannot predissociate. This leaves the field-induced dissociation in the dipole magnet (Sec. III B) as the only available mechanism. For this to occur, the molecules have to be laser-excited to bound levels just below the lower fine-structure limit which possess a sufficiently long radiative lifetime to reach the magnet in spite of the time-of-flight of about 1 \(\mu\)s. This requirement allows one to distinguish predissociation and field-induced features by the observed widths: Given the experimental resolution of about 0.5 cm\(^{-1}\), a resonance with an observable broadening must have a lifetime shorter than 10 ps, and therefore cannot be due to field dissociation, but only to true predissociation. We therefore required all broadened features to lie within the allowed energy windows, or slightly above to account for shape resonances.

This is illustrated for the resonance group assigned to \(J^* = 5\) in Fig. 5, by using the window allowed by Eq. (14) and assuming \(D_0 = 32,948\) cm\(^{-1}\). The broad steep edge at 32,532 cm\(^{-1}\) cannot be due to field dissociation and serves as an upper limit for the lower threshold. A lower limit for the upper threshold is defined by requiring resonances above this limit to lie within the expected height of the centrifugal barrier (4 cm\(^{-1}\) for \(J^* = 5\); see Sec. IV C 3). This fixes the thresholds within about 1 cm\(^{-1}\). The strong narrow resonance at 32,524 cm\(^{-1}\) lies below this allowed window and is thus attributed to field dissociation.

The value \(D_0 = 32,948\) cm\(^{-1}\) leads to an equally good match for the other resonance groups. Assuming an uncertainty of about 1 cm\(^{-1}\) in matching the window pattern to the spectrum, and adding the uncertainty of the energy scale (\(\pm 1.1\) cm\(^{-1}\); see Sec. III D), the uncertainty of this \(D_0\) value is about \(\pm 2\) cm\(^{-1}\). This preliminary value will be confirmed and refined by analyzing the spectral structure within the groups (Secs. IV C 2 and IV D 4). With the known dissociation energy, the assignment of initial states by identification of the resonance groups is straightforward except for \(J^* \approx 2\) where the groups overlap because \(E_{J^*+1} - E_{J^*} \approx \Delta E_{\text{so}}\) (Fig. 4).

C. Assignment of near-threshold resonances: Conventional approach

As explained in Sec. II, the resonance patterns within the groups reflect the level structure and predissociation dynamics of the final states between the fine-structure states of the \(+2\) ion.\(^{12}\) In this section, a standard spectroscopic analysis is applied as far as possible: By identification of branches and least-squares fitting of line positions, the most prominent features can be assigned. Although the full quantitative analysis requires the close-coupling approach described in Sec. IV D, the conventional analysis is physically instructive, and the concepts introduced are also important for the close-coupling analysis.

1. Asymptotic energies

Since the initial levels of most resonances are known, the spectrum can be corrected for the known initial energies (Table II) and for the dissociation energy \(D_0 = 32,948\) cm\(^{-1}\) (see above) by defining the asymptotic energy of a resonance with wave number \(\bar{v}\) and initial level \(X^1 \Sigma^+ (v'' = 0, J''\) to be

\[
\bar{\nu}^\prime = \bar{\nu} + E_{J''} - D_0.
\] (22)

The asymptotic energy thus corresponds to the energy of the final level with respect to the lower threshold \(+2P_{1/2}\) + H, that is, to the relative kinetic energy of the fragments if the \(+2\) fragment is in the lower fine-structure state.

As a starting point, we identified 66 peaklike features in the spectrum and fitted Gaussian profiles to determine their approximate positions, widths, and areas. Gaussians were chosen for simplicity because most broad peaks appear quite irregular and anyway cannot be described by analytical line shapes (Fig. 5). All peak positions, intensities, and widths appear in Table VI (Sec. IV D 6).

The asymptotic energies of most resonances are found to lie between the fine-structure levels of \(+2\) at 0 and 63.42 cm\(^{-1}\). A practical tool to spot the structure within the resonance groups is a plot of the asymptotic energies of all resonances as a function of \(J^* (J^*+1)\) because rotational sublevels \(J^*\) of the same vibrational level \(v''\) will fit into a pattern if one assumes an energy dependence of \(E_{v''} + B_v J^* (J^* + 1)\). Figure 6 shows this plot for the current spectrum, with resonance widths indicated by error bars.

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Figure 6. Asymptotic energies of resonances as a function of $J''(J''+1)$, with the linewidths represented by error bars. The two thresholds are shown as horizontal lines. The allowed windows for $J''=0,1,2$ are mutually overlapped by the neighboring energy windows, yielding a corresponding ambiguity and hence a multiple $J''$-assignment for the resonances marked by the shaded areas. Transitions forming straight line patterns indicate branches [(Q1, P1, R1), (Q2, P2, R2, Q3) at $J''=7-9$, not shown)]. Pairs of P and R transitions (dashed lines) indicate e levels (empty circles when shifted to $J''=J'$), Q transitions indicate f levels, for which the spectroscopic constants have been determined by a fit (full lines).

In this plot, an $R(J''=J'-1)$ transition and the corresponding $P(J''=J'+1)$ transition to the same final state $J'$ will appear as two points at $J''=J'\pm 1$ at the same asymptotic energy. Since both transitions share the same final state, the peaks must have the same width and shape. Furthermore, the final state must have e parity because the $X\,^1\Sigma^+$ initial state has e parity (Sec. II A), and a dipole transition requires $e\leftrightarrow e$ for P and R transitions. If there are several e upper rotational levels belonging to the same vibrational level, the corresponding points will approximately form a straight line when plotted as function of $J''(J''+1)$, or when shifted to $J''=J'$ in Fig. 6. In contrast, a given final rotational level $J''=J'$ of f parity can be reached only by a single $Q(J'')$ transition, and f rotational sublevels of the same vibrational level must form a straight line in Fig. 6 because $J'=J''$.

Following these rules, we identified three Q branches (Q1, Q2, Q3 in Fig. 6), each one marking a vibrational level with f parity. Another branch (Q4) appears for $J''=7-9$. By fitting the asymptotic energies to $E_{v'',f}+B_{v''}J''(J''+1)$ (full lines in Fig. 6), we found the vibrational energies and rotational constants in Table III. There are also two R and two P branches (R1, R2, P1, P2) jointly marking two vibrational levels of e parity which lie very close in energy (dashed lines and empty circles in Fig. 6).

### 2. A $^1\Pi$ resonances

Theory predicts the strongest transitions to go to quasibound levels of A $^1\Pi$ character, and the Q branch to be stronger than the R and P branch (as expected from the Hön–London $PQR$ intensity ratio of about 1:2:1 for a $^1\Pi^3-\Sigma^3$ transition).

The resonances that have been grouped into vibrational levels with the help of Fig. 6 happen to be the most pronounced features of the spectrum. The strong resonance at 32 576 cm$^{-1}$ (Fig. 5) belongs to the $Q_1$ branch, for example. We therefore assigned the four Q branches in Table III to adjacent vibrational levels of the adiabatic A $^1\Pi_J$ curve that correlates to the upper fine-structure limit in Fig. 2(b). The calculations predict the levels A $^1\Pi_J (v'=12-14)$ to lie between the fine-structure limits for low rotation ($J'\leq 6$) and the next lower level A $^1\Pi_J (v'=11)$ to appear for higher rotation ($J'\geq 7$). The four branches $Q_{1-4}$ show exactly this behavior, so they are assigned absolute vibrational quantum numbers 11–14 (Table III), although this assignment will remain tentative until the implications of the new D$_0$ value for the total depth of the A $^1\Pi$ curve have been discussed in Sec. IV C 5.

In order to check if all four levels can belong to the same potential, we applied the Le Roy–Bernstein formula which relates the energies $E_{v',f}$ of the highest vibrational levels in a potential to its asymptote $V_{\text{lim}}$, to the (generally noninteger) effective vibrational index $v_D$ at threshold, and to the leading term in the long-range expansion of the potential. For C$^+(2P) + \text{H}(2S)$ this term is $-C_4/r^4$. The coefficient $C_4 = 38.720$ cm$^{-1}$ Å$^4$ is known exactly from the polarizability of the H atom.

This is strictly valid only for the BO potentials, but we assumed the adiabatic A $^1\Pi_J$ potential in Fig. 2 to have the same long-range form. The Le Roy–Bernstein formula then reads

$$E_{v'} = V_{\text{lim}} - X_4(v_D - v')^4, \quad X_4 = 0.4013 \text{ cm}^{-1},$$

where the constant $X_4$ was calculated from $C_4$.

Figure 7 shows the measured vibrational energies in a least-squares fit to Eq. (23), with $V_{\text{lim}}$ and $v_D$ as free parameters. The good agreement shows that the four states indeed belong to a single potential with the expected long-range form. The fit yields $V_{\text{lim}} = 63.1$ cm$^{-1}$ for the asymptote, and thus for the upper fine-structure limit on the asymptotic energy scale. Since this limit should lie at $\Delta E_{v''} = 63.42$ cm$^{-1}$, we conclude that the asymptotic energies attributed to the peaks by Eq. (22) are correct, which confirms the value derived for $D_0$ in Sec. IV B. The vibrational index $v_D$ of the adiabatic A $^1\Pi_J$ curve is 15.33(2) according to the fit. The vibrational defect, i.e., the fractional part of the vibrational index, is 0.33(2). Actually, the last bound level should be $v' = 15$, with a binding energy of only $4.8 \times 10^{-3}$ cm$^{-1}$. It is difficult to predict if this level would persist if a rotational

### Table III. Vibrational energies, rotational constants, and assignment of the $f$ vibrational states identified via the $Q$ branches in Fig. 6 ($Q_5$ is not shown in Fig. 6).

<table>
<thead>
<tr>
<th>Branch</th>
<th>$E_{v',f}$ (cm$^{-1}$)</th>
<th>$B_{v',f}$ (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_1$</td>
<td>12.5(7)</td>
<td>1.05(3)</td>
<td>$^1\Pi'_J (v'=12)$</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>52.1(7)</td>
<td>0.40(2)</td>
<td>$^1\Pi'_J (v'=13)$</td>
</tr>
<tr>
<td>$Q_3$</td>
<td>61 (1)</td>
<td>0.11(1)</td>
<td>$^1\Pi'_J (v'=14)$</td>
</tr>
<tr>
<td>$Q_4$</td>
<td>$-73(3)$</td>
<td>1.50(4)</td>
<td>$^1\Pi'_J (v'=11)$</td>
</tr>
</tbody>
</table>
energy term is added to the potential. In any case, it would have extreme long-range character. The last observed level \(v' = 14\) already has the maximum of its radial probability around \(r = 10 \text{ Å}\), and a probability for \(r < 5 \text{ Å}\) of only 0.02, as we found from computing the radial wave function with the program LEVEL (Ref. 48) in the adiabatic \(A^1 \Pi^+\) potential scaled to have \(v_D = 15.33\).

The two vibrational series of \(e\) parity that are nearly parallel to the \(Q_1\) series and are marked with empty circles in Fig. 6 are more difficult to assign. One of them coincides with the \(A^1 \Pi_2^+ (v' = 12)\) levels within 1 cm\(^{-1}\), the other lies a few cm\(^{-1}\) higher, the distance slightly increasing with \(J\). Both have almost equal strength and width. Two representative \(P_1\) and \(P_2\) peaks can be seen in Fig. 5 at 32 570 and 32 565 cm\(^{-1}\), respectively. In order to predict the position of the \(A^1 \Pi_2^+ (v' = 12)\) vibrational states from the assigned \(A^1 \Pi_1^+ (v' = 12)\) states, we estimated the \(\Lambda\) doubling between the adiabatic \(A^1 \Pi_1^+\) and \(A^1 \Pi_2^+\) potentials from the matrix element in Table I and the distance to the perturbing \(X^1 \Sigma^+\) curve at the relevant internuclear distances, following Ref. 49. As the expected splitting is a few cm\(^{-1}\), rather than \(< 1 \text{ cm}^{-1}\), we assigned the upper series (the branches \(R_1\) and \(P_1\)) to the \(A^1 \Pi_1^+ (v' = 12)\) state.

### 3. Resonances outside the fine-structure window

Figure 6 displays a number of features with asymptotic energies below or above the fine-structure window. At \(J'' = 0 -- 2\), where the resonance groups overlap, some of the peaks come back into an allowed window when assigned to another \(J''\) value (hatched regions), but for higher \(J''\), resonances occur up to \(-12 \text{ cm}^{-1}\) below, and 17 cm\(^{-1}\) above the window (for \(J'' = 8\), not shown in Fig. 6). We now need to estimate quantitatively whether all these features can result from field dissociation in the magnet or be shape resonances, as invoked in Sec. IV B.

If we assume the adiabatic potentials (Fig. 2) to have the long-range form \(-C_4/r^4\) and approximate their \(J''\)-dependence by adding \(\hbar^2 J'(J' + 1)/(2\mu r^2)\), we find

\[
V_{\text{max}} = \frac{1}{4} \frac{\hbar^2}{2\mu} \left[ f(J'(J' + 1) + 1) \right]^2 C_4
\]

for the height of the rotational barrier. All resonances above the upper asymptote lie within this limit if they are assumed to be \(R\) branch resonances (\(J' = J'' + 1\)).

We estimated the maximum binding energy sensitive to field dissociation in the dipole magnet as follows:

As the charge of the weakly bound \(\text{CH}^+\) molecule can be regarded as attached to the \(\text{C}^+\) ion, the electric field \((E = 120 \text{ kV/cm})\) produces a force of \(eE\mu/m_c^+\) in the rest frame of the ion. If the molecule is oriented such that this force counteracts the binding force, all potential curves shift by

\[
-erE\mu/m_c^+ = -r \cdot 0.74 \text{ cm}^{-1} \text{ Å}^{-1}
\]

In the \(-C_4/r^4\) potential, this additional term can cause levels up to 12 cm\(^{-1}\) below threshold to dissociate. This agrees very well with the asymptotic energy range of the observed resonances below the lower fine-structure limit (Fig. 6).

### 4. Widths of the \(A^1 \Pi^+\) resonances

Rotational sublevels of the same vibrational state are observed to have similar widths. The resonances assigned to \(A^1 \Pi_1^+ (v' = 12)\) show widths 1.5 -- 2 cm\(^{-1}\). The respective lines of \(A^1 \Pi_1^+ (v' = 12)\) are slightly broader (2 -- 3 cm\(^{-1}\)). The \(A^1 \Pi_1^+ (v' = 11)\) widths are about 4 -- 5 cm\(^{-1}\), and the \(A^1 \Pi_1^+ (v' = 13--14)\) widths are less than the experimental resolution.

The observed widths are entirely due to predissociation because the radiative decay back to the \(X^1 \Sigma^+\) state was estimated to contribute only \(5 \times 10^{-7} \text{ cm}^{-1}\). The fact that the predissociation widths are smallest for the least bound states agrees with theoretical predictions.

The stronger broadening of the \(A^1 \Pi e\) levels compared to the \(f\) levels is predicted by theory as well, and can be explained by the rotational coupling of the \(A^1 \Pi\) state to the \(X^1 \Sigma^+\) state that exists in the \(e\) block, but not in the \(f\) block (Table I).

### 5. Discussion of the conventional analysis

The results obtained so far are limited to the dissociation energy \(D_0\), the energies and widths of the \(A^1 \Pi\) rovibrational levels between the fine-structure states of the \(\text{C}^+\) ion, and the vibrational defect of the adiabatic \(A^1 \Pi^+\) potential. The new value \(D_0 = 32.948 \pm 0.2 \text{ cm}^{-1}\) differs slightly from the previous value 32.907(23) of Helm.\(^{18}\) The underestimation of \(D_0\) by Helm et al.\(^{18}\) probably arises from their assumption that the observed \(A^1 \Pi\) shape resonances predissociate entirely to the upper fine-structure limit to which the \(A^1 \Pi\) curve correlates adiabatically. But later calculations revealed that these resonances could as well dissociate to the lower limit because of radial coupling between the adiabatic curves.

According to the new \(D_0\) value, the \(A^1 \Pi\) potential is about 0.4\% deeper than assumed in the calculations, on which the above assignment of absolute vibrational quantum numbers of the \(A^1 \Pi\) resonances was based. This modification cannot change the quantum numbers of these levels by one unit, as was verified from trial calculations using the program LEVEL.\(^{48}\) Therefore, the vibrational quantum numbers assigned above (Sec. IV C 2) should be correct.
The shape of the $A^1\Pi$ curve was not altered in the calculations because it is relatively well characterized by spectroscopic data.

The foregoing conventional analysis of the $A^1\Pi$ spectrum is consistent, the results agree with theoretical predictions, and no line shifts due to perturbations are seen at the current precision of measurement. On the other hand, only 28 peaks out of a total of 66 peaks have been identified. Assigning the remaining features is difficult for two reasons: First, most of the additional features are weaker than the $A^1\Pi$ resonances, so that some rotational sublevels of a vibrational state are not detected. As a result, only scattered points appear in Fig. 6, instead of clear branches. Second, even if there were clear branches, the assignment of these resonances to specific adiabatic curves could only be guessed. The only example of complete non-$A^1\Pi$ branches are the $K_2$ and $P_2$ branch in Fig. 6 that mark a series of $e$ rotational levels. The underlying vibrational state cannot arise from the $A^1\Pi^J_0$ adiabatic potential because it would lie too close to $A^1\Pi^J_e$ ($v' = 12$) and thus violate the Le Roy–Bernstein formula. Given the nonadiabatic couplings, this state can in principle be due to any of the other $e$ curves correlating to the upper limit in Fig. 2(a): $c^\Sigma^+_1 \epsilon$, $a^3\Pi^+_2$, or $a^3\Pi^0_1$.

Even if yet unassigned, the mere existence of non-$A^1\Pi$ features is a multichannel effect predicted by the close-coupling calculation. Furthermore, the experimental spectrum qualitatively resembles theory in that a large variety of spectral shapes is observed. This qualitative agreement shows that multichannel effects must be fully taken into account in the further analysis.

### D. Assignment of near-threshold resonances: Close-coupling model

Despite the good qualitative agreement, the original close-coupling spectrum calculated by Williams and Freed differs significantly from the experimental data when a quantitative comparison is made. Actually, only the positions of the $A^1\Pi$ features roughly correspond, the remaining structure appears different. However, as already pointed out in Ref. 12, the calculation cannot be expected to be quantitatively correct because of the uncertainty of the input BO potentials and the high sensitivity that is found in the calculated spectrum when the details of these curves are changed.

Hanrath and Peyerimhoff provided us with new $ab$ initio potentials with an estimated accuracy of about 100 cm$^{-1}$. But because of the strong sensitivity to the underlying BO potentials even this could not be expected to be good enough to successfully model the near-threshold spectrum. The only solution thus was to iteratively perform close-coupling calculations and to tune the $ab$ initio potentials in order to reproduce the observed spectrum.

#### 1. Parameterization of the BO potentials

In order to choose effective tuning parameters, we made use of the fact that the coupling between the components of the multichannel wave function becomes important only at large $r \geq 3$ Å. The shape of the BO potentials at small $r < 3$ Å is not critical as long as they provide the correct phase of the respective wave function components upon entry into the coupling region. In contrast, the long-range part must be accurate because it influences both the coupling and the energy dependence of the final continuum wave function.

Consequently, we divided each BO potential $U_{\Lambda,S}$ into an inner part $U_{\Lambda,S}^{in}$ and a long-range part $U_{\Lambda,S}^{lr}$

$$U_{\Lambda,S}(r) = U_{\Lambda,S}^{in}(r) + U_{\Lambda,S}^{lr}(r)$$

with the boundary handled by the switching function

$$f_{sw}(r) = (e^{\alpha(r-r_{sw})} + 1)^{-1}$$

at some matching point $r_{sw} \leq 3$ Å, to be specified below.

For the long-range potentials, the only theoretical study is the early work of Harel, who numerically computed the induction, dispersion, and exchange energies and fitted the resulting curves to analytical functions of the form $A_1 e^{\gamma r} - A_2 e^{-\gamma r}$. Comparing these long-range potentials to the new $ab$ initio potentials reveals substantial disagreement (dashed lines versus dots in Fig. 8). The $\Sigma$ curves match well, but the $ab$ initio $\Pi$ states are more attractive and exhibit a much larger exchange splitting than those of Harel. The estimated accuracy of the $ab$ initio calculation is about 100 cm$^{-1}$, which we trust because (1) the calculated $X^1\Sigma^+$ curve indeed gives the correct dissociation energy to about this precision, (2) the empirically determined $A^1\Pi$ curve of Freed et al.

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For use in the model potentials [Eq. (25)] an analytical form for the $U_{\Lambda,S}^{lr}$ was needed. We first considered trying to refit each $ab$ initio potential with the function used by Harel, but this would have introduced many empirical parameters. These would have made the fit unreliable at large $r \geq 3.5$ Å, where the uncertainty of the calculations is larger than the separation of the curves, and it would have hindered...
TABLE IV. Parameters describing the long-range BO potentials via Eqs. (27)–(29). C₂ is known, C₆ and κ were estimated (Secs. IV D 1 and Appendix). C₄, κ₁, and Aₑxₐ were determined by a least-squares fit to the ab initio potentials (Ref. 27). κ₁ was finally refitted together with the well depths to match the experimental spectrum.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A = 0 (Σ states)</th>
<th>A = 1 (Π states)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂ (cm⁻¹ Å²)</td>
<td>3.872 × 10⁴</td>
<td>3.872 × 10⁴</td>
</tr>
<tr>
<td>C₆ (cm⁻¹ Å²)</td>
<td>4.37 × 10³</td>
<td>1.07 × 10⁴</td>
</tr>
<tr>
<td>C₈ (cm⁻¹ Å²)</td>
<td>1.60 × 10⁴</td>
<td>3.30 × 10⁴</td>
</tr>
<tr>
<td>κ</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>κ₁</td>
<td>1.94 (final: 1.3507)</td>
<td></td>
</tr>
<tr>
<td>Aₑxₐ (cm⁻¹)</td>
<td>-3340</td>
<td>1040</td>
</tr>
</tbody>
</table>

any physically consistent tuning of the long-range part. Thus the earlier long-range treatment had to be revised in order to develop a more robust analytical form with physically meaningful parameters.

The long-range potentials can be written as a sum of a mean induction/dispersion potential and a singlet–triplet exchange splitting,

\[ U_{l,t}(r) = U_{id}(r) \pm \Delta U_{ex}(r), \tag{27} \]

with the upper (lower) sign for \( S = 0 (1) \). The induction and dispersion part is approximated by the sum

\[ U_{id}(r) = \sum_{n=4,6,8} -\frac{C_n}{r^n}, \tag{28} \]

where \( C_2 \) is known exactly. The \( C_6 \) coefficients, which contain induction and dispersion terms, have not been accurately determined before, and are thus derived in the Appendix. Empirical \( C_8 \) coefficients were determined by least-squares fitting Eq. (28) to the average value of the \( 1^3\Pi \) and \( 1^3\Sigma \) points at \( r > 2.7 \) Å. All \( C_{4,6,8} \) coefficients are listed in Table IV.

For smaller \( r \), Eq. (28) failed to match the ab initio data. We thus set \( r_{sw} = 2.7 \) Å in Eq. (26), and \( \alpha \) such that \( f_{sw}(R) \) reaches 90% at \( r_{sw} \approx 0.15 \) Å. With this boundary, the coupling region is entirely defined by the long-range potentials.

The singlet–triplet splitting \( \Delta U_{ex}(r) \) is more difficult to describe. Although formulas exist that relate the long-range exchange splitting in a molecule to the square root of the ionization potentials of the two atoms and the asymptotic form of the wave functions of the outer electrons, \(^{51}\) none of these expressions is strictly valid for CH \(^1\): The ionization potentials are such that the parameters \( \beta_{C^+} = \sqrt{2m_J C^+} / \hbar = 2.53 \) Å⁻¹ and \( \beta_{H^+} = \sqrt{2m_J H^+} / \hbar = 1.89 \) Å⁻¹ neither satisfy \( \beta_{C^+} > \beta_{H^+} \) (symmetric case) nor \( \beta_{C^+} > \beta_{H^+} \) (strongly asymmetric case) at the internuclear distance of interest (\( r > 2.7 \) Å). \(^{51}\)

Lacking a rigorously valid expression, we assumed the exchange splitting to have the simple functional form for the symmetric case, \(^{51}\)

\[ \Delta U_{ex}(r) = A_{\infty}(r_{sw}) \cdot \frac{r}{r_{sw}}^{\kappa}\, e^{-\kappa(r-r_{sw})}, \tag{29} \]

with the normalization to \( r_{sw} \) included for convenience. The exponential parameter \( \kappa \) is bracketed by the values it would have in the asymmetric and the symmetric limiting case, respectively. \(^{51}\)

\[ 2\beta_{H^+} \leq \kappa \leq \beta_{H^+} + \beta_{C^+}, \tag{30} \]

yielding \( 3.78 \) Å⁻¹ \( \leq \kappa \leq 4.42 \) Å⁻¹. We chose \( \kappa = 4 \) Å⁻¹. Furthermore, the expressions for \( \kappa \) generally include a term \(-\Lambda\). \(^{51}\) We thus required \( \kappa_0 = \kappa_1 + 1 \). Equation (29) was then fitted to the \( \Sigma \) and \( \Pi \) ab initio exchange splittings at \( R > 2.7 \) Å, with \( A_{\infty}, A_{\infty}', \) and \( \kappa_1 \) as free parameters. The resulting values are listed in Table IV.

The new long-range potentials defined by Eqs. (28) and (29) match the ab initio points very well (see Fig. 8). Note that the \( X^1\Sigma^+ \) state inevitably crosses the \( \Pi \) states, because the exchange splittings vanish exponentially so that the energy ordering at sufficiently large \( r \) is determined by the larger \( C_6 \) value of the \( \Pi \) curves.

Now consider the inner parts of the potentials. To model \( U_{in}(r) \), the ab initio potentials \(^{27}\) were fitted to purely empirical functions. In order to tune the phases of the respective multichannel wave function components, the depths of the potentials were changed by adding or subtracting between 0.9 Å and 2.0 Å a polynomial in \( r \). The mostly repulsive \( c^3\Sigma^+ \) state, for which such a change is irrelevant for the spectrum considered here, was tuned by adding or subtracting around 3 Å. The potential tuning scheme is visualized in Fig. 9.

The effects of the changes were monitored by numerically computing the vibrational indices \( v_D \) from the semiclassical phase integrals,

\[ v_D + \frac{1}{2} = \frac{1}{\pi} \int_{U(r) < 0} dr \sqrt{-\frac{2\mu}{\hbar^2} U(r)}, \tag{31} \]
for the BO potentials. The multichannel wave function in the long-range coupling region is not affected if the phase that one of its components accumulates before the coupling region changes by an integer multiple of $\pi$. The absolute numbers of vibrational levels in the BO potentials (the integer parts of $v_D$) are thus expected to have almost no influence on the near-threshold photodissociation spectrum. In principle, each set of trial potentials can thus be fully characterized by the fixed long-range part and just the vibrational defects (the fractional parts of $v_D$), except for the $^3\Sigma^+$ state whose well lies in the coupling region.

### 2. Computational method

A detailed description of the close-coupling code used in this work can be found in Ref. 12. The code can compute the photodissociation cross section from an initial bound state $X^1\Sigma^+\left(v''=J''\right)$ of the molecule to a final continuum state of asymptotic energy $E_{as}$, angular momentum $J$ and the atomic quantum numbers specified in Eq. (11). The calculation can be viewed as consisting of two parts: First, a scattering calculation solves the coupled radial equations for the continuum multichannel wave function. The potential matrix is taken as given in Table I, with the underlying BO potentials calculated on a grid following the above model, and represented in the code by cubic splines. Next the dipole transition matrix element is evaluated between the initial bound $X^1\Sigma^+$ state and the $A^1\Pi$ component of the previously calculated multichannel scattering wave function. For this second part, we used the theoretical dipole transition moment function of Elander, and fixed $X^1\Sigma^+\left(v''=0,J''\right)$ vibrational wave functions. These vibrational wave functions were calculated only once (in the unchanged ab initio $X^1\Sigma^+$ potential) and thus were not affected by the changes made in the BO potentials during the simulations.

In order to calculate the photodissociation cross section for a given initial state $X^1\Sigma^+\left(v''=0,J''\right)$, asymptotic energy $E_{as}$ and final $J' \neq 1$, the partial cross sections of all open channels were added because the experiment did not distinguish between final states. The calculated spectra thus include dissociation into $C^+\left(P_{1/2}\right)$ as well as into $C^+\left(S_{1/2}\right)$ fragments, the latter contributing only for $E_{as} > \Delta E_{1s}$. Finally, $P$, $Q$, and $R$ contributions were added ($J' = J''-1,J'',J''+1$) to get the total photodissociation cross section expected from a single initial state $X^1\Sigma^+\left(v''=0,J''\right)$.

### 3. Determination of vibrational defects

To find a set of model potentials that would reproduce the experimental spectrum, we began by calculating the photodissociation spectrum with the above model potentials, using the original (ab initio) well depths, for a single $J''$ group. The resulting spectrum differed substantially from the experimental one. Before making changes to the model potentials, though, we had to assign the theoretical spectrum, to be able to choose the next model potentials systematically. The assignment was done as described in Ref. 12. The defects of the four BO potentials were increased or reduced by small amounts. Resonances which then shifted to lower or higher energies upon the change of a particular BO potential were assigned to that electronic state, as if they were rovibrational levels in the adiabatic potential curves correlating to the upper limit in Fig. 2. As expected, changing the effective vibrational index $v_D$ of a potential by exactly one unit (thus keeping its vibrational defect constant) left the structure of the simulated spectra unchanged.

First, we identified the $A^1\Pi$ resonances in the theoretical trial spectrum. Then, we modified the defect of the $A^1\Pi$ well so that these peaks matched the experimentally observed $A^1\Pi$ resonances already identified by the conventional analysis. Adjusting the $a^3\Pi$, $c^3\Sigma^+$, and $X^1\Sigma^+$ depths was more difficult because no features from these curves had been assigned. These defects were systematically varied in coarse steps of the order of 0.1 vibrational levels, up to a total change in $v_D$ of one level. All possible combinations were simulated and compared to the experimental spectrum. This showed that the shapes and widths of the assigned $A^1\Pi$ resonances, but not their positions, depended critically on the $a^3\Pi$ and $c^3\Sigma^+$ vibrational defects [the $X^1\Sigma^+$ state does not exist in the $f$ parity block (Fig. 2)]. We therefore focused on reproducing these shapes by tuning the $a^3\Pi$ and $c^3\Sigma^+$ BO potentials, which approximately fixed their vibrational defects and allowed assignment of additional features to these curves. Then, the remaining features were optimized by varying just the $X^1\Sigma^+$ curve. Finally, slight readjustments were made to all four defects.

The determination of defects is illustrated in Fig. 10. Figure 10(a) shows the measured resonance group of $J''=5$ already displayed in Fig. 5, but after subtraction of the continuous background, on the asymptotic energy scale, and smoothed as described in Sec. III D. Superimposed we see the corresponding theoretical spectrum, with all defects optimized, scaled to match the measured spectrum and calculated on a 0.1 cm$^{-1}$ grid. Figure 10(b) shows the theoretical $P$, $Q$, and $R$ contributions separately. According to the model spectrum, the strong peak detected around 45 cm$^{-1}$ is the $Q$ branch peak $C$, the hardly significant peak at 24 cm$^{-1}$ corresponds to the $Q$ resonance $A$, and the broad double peak at 35 and 40 cm$^{-1}$ contains a $P$ branch as well as a $Q$ branch contribution ($B$). The predicted $Q$ branch resonance $D$ is too narrow to be observed experimentally.

The sensitivity of the theoretical spectrum to variations of the defects is demonstrated in Figs. 10(c)–10(f). For clarity, only the $Q$ branch contribution and the total ($P$, $Q$, and $R$) spectrum are shown. In Fig. 10(c), the vibrational index $v_D$ of the $A^1\Pi$ potential has been increased from its optimum value 15.20 to 15.31. Compared to Fig. 10(b), the strong resonance $C$ has shifted to lower energies, has narrowed, and mixed with peak $B$. Resonances $A$, $B$, and $D$ have stayed approximately at the same place. We therefore assigned $C$ to the $A^1\Pi$ adiabatic potential, confirming the previous conventional analysis (Sec. IV C 2). In Fig. 10(d), the $A^1\Pi$ vibrational index has been restored to its optimum value, but the $a^3\Pi$ defect has been increased by 0.11, causing features $A$ and $B$ to shift to lower energies, and $C$ to broaden significantly in comparison to Fig. 10(b). In Fig. 10(e), the shallow $c^3\Sigma^+$ potential has been deepened by 0.15. Features $A$ and $B$ have shifted similarly to Fig. 10(d), and the feature $D$ has also shifted to lower energy. As $A$, $B$,
and D are Q features, they must mark quasibound levels of the \( a^1\Pi_g^0 \), \( c^1\Sigma^+_g \) or \( c^1\Sigma^+_u \) adiabatic curves in Fig. 2(b), but they are not as easy to assign as C because they react both to the \( a^1\Pi \) and to the \( c^3\Sigma^+ \) potential. In such cases, we assigned the features by taking into account the other \( J'' \) groups as well, by performing single-channel calculations\(^{24} \) in the adiabatic potentials of Fig. 2, estimating splittings, etc. Here, A is assigned to \( a^1\Pi_g^0 \), and B and D are assigned to \( c^3\Sigma^+_u \) and \( c^3\Sigma^+_g \) (Sec. IV D 6). Finally, the vibrational defect of the \( X^1\Sigma^+ \) potential has been decreased by 0.19 [part (f)]. The Q contribution stays the same as in part (b) because the \( X^1\Sigma^+ \) potential does not exist in the \( f \) parity block, but the total spectrum is nevertheless different from (b) due to changes of the \( P \) and \( R \) contributions.

The comparison of Figs. 10(a)–10(b) shows that the theoretical spectrum matches the experimental spectrum well if the vibrational defects are set to specific values. Given the large number of experimental features which are reproduced with a minimum of free parameters, we conclude that the close-coupling model, which links the BO potentials to the photodissociation spectrum, must be quantitatively correct within the precision of the experiment. Furthermore, parts (c)–(f) of Fig. 10 demonstrate that the vibrational defects affect the spectrum in different ways (so that modifications cannot compensate one another), and that the allowed variations of the defects consistent with the data are small. From this fact, together with the correctness of the model, we conclude that the experimental spectrum allows us to uniquely determine the vibrational defects of all four involved BO potentials.

4. Direct fit to the complete spectrum

So far, the vibrational defects have been shown to be consistent with a single \( J'' \) resonance group. When calculating other resonance groups with the same defects, we also found good agreement, but not as good as for the first group. Manually adjusting the defects to optimize several groups at the same time turned out to be too complex, especially if slight changes of \( D_0 \) were allowed. Furthermore, judging the quality of the simulation just by visual inspection appeared somehow arbitrary. Therefore, we performed a nonlinear least-squares fit of the model spectrum to the experimental data, consisting of all measured points in Fig. 4, weighted according to their errors, without smoothing, and without the superimposed \( b^3\Sigma^--a^1\Pi \) lines.

As free parameters for the \( X^1\Sigma^+ , A^1\Pi \), and \( a^3\Pi \) BO potentials, we used the coefficients of the polynomial to be added or subtracted between 0.9 Å and 2.0 Å. These parameters are directly linked to the well depths. In contrast to the previous simulations, the \( c^3\Sigma^+ \) state was not tuned by adding/subtracting to the long-range \( c^3\Sigma^+ \) curve given by the long-range analytical model of Eqs. (27)–(29), but by adjusting the long-range model itself to keep the potentials physically consistent. We chose the empirical parameter \( \kappa_1 \) which had a value of 1.94 according to the fit to the \( ab \) initio points (see Sec. IV D 1), but was not well-constrained by this fit. The \( c^3\Sigma^+ \) vibrational defect could be roughly predefined by setting \( \kappa_1 = 1.35 \), which did not significantly reduce the agreement with the calculated points in Fig. 8. The other defects were then preadjusted via the well depths. Note that \( \kappa_1 \) influences not only the \( c^3\Sigma^+ \) state but all BO potentials. This correlation was acceptable since it would be handled by the least-squares fit.

The fitting code was built around a Levenberg–Marquardt fitting routine.\(^{55} \) At each iteration, all contributions \( \sigma_f(\tilde{v}_n) \) were calculated as a function of asymptotic energy on a 0.25 cm\(^{-1} \) grid, convoluted with the experimental resolution (0.5 cm\(^{-1} \)) and splined for subsequent interpolation. The full spectrum was then constructed by shifting, scaling and superimposing all groups,

\[
\sigma(\tilde{v}) = \sum_{j'=0}^{9} p_{j'} \sigma_{j'}(\tilde{v} + E_{j'} - D_0). \tag{32}
\]

The group amplitudes \( p_{j'} \) were treated as free parameters, and also the dissociation energy to permit small energy shifts of the spectrum as a whole. The relative positions of the
groups were fixed via the known $E_{Jn}$ values (Table II). Since the fitting routine required the derivatives of the theoretical spectrum with respect to the parameters, these were determined numerically by slightly changing the potentials and repeating the close-coupling calculation (for the potential parameters), or analytically via Eq. (32) (for $p_{Jn}$ and $D_0$).

The quality of the fit depended critically on the initial values of the parameters. Furthermore, the results were better when the fit was started with only a few groups, and then continued with more data. A few strong narrow peaks (with widths of 0.5 cm$^{-1}$, i.e., experimental resolution) had to be excluded because in these cases, shifts of about 1 cm$^{-1}$ between the observed and calculated peaks were enough for them to lose overlap, making it impossible for the fitting routine to improve the fit. Practically, the exclusion was achieved by giving small weights to the corresponding data points in the spectrum. In other cases, features got higher weights in order to force the fit into the required direction. These difficulties are understandable because the close-coupling model is an extremely complicated fitting function, and because any individual spectral detail only makes a very small difference in the total $\chi^2$.

The best fit to the complete spectrum is shown in Fig. 11, with the groups $J'' = 2,3,4,$ and $8$ as examples. The close-coupling model describes the experimental data very well. A few peaks are not accounted for (marked with empty triangles), but these lie just below the lower bound of some of the allowed windows and are also narrow enough to be attributed to field dissociation. The only broad peak which is not reproduced (near 32 911 cm$^{-1}$ in $J'' = 2$) probably consists of two overlapping narrow field dissociation peaks. The agreement between theory and experiment includes resonance energies, shapes, and relative strengths, and extends also across the experimental data not shown in Figs. 11 or 10.

The $\chi^2$ per degree of freedom of the fit being about 2, the fit cannot be considered to be very good on strict numerical grounds. But this is partly due to the fact that the standard uncertainty of the energy axis (1.1 cm$^{-1}$, Sec. III D) was not taken into account when calculating $\chi^2$. For example, the small energy shift between experiment and theory in the group $J'' = 4$ can be due to this uncertainty.

For $D_0$, the fit yielded 32 946.7 cm$^{-1}$. This number agrees with the previous value from the conventional analysis, 32 948 ± 2 cm$^{-1}$, but the new value is more precise because it is based on all features in the spectrum via a quantitatively correct model. The formal uncertainty of $D_0$ according to the fit can be neglected compared to the 1.1 cm$^{-1}$ uncertainty of the underlying experimental energy scale. We thus state (32 946.7 ± 1.1) cm$^{-1}$ for the dissociation energy of CH$^+$. The fitted group amplitudes $p_{Jn}$ are in principle proportional to the population of the initial $J''$ states and could be used to infer the rotational distribution of the stored CH$^+$ molecules more precisely than previously,26 where the theoretical cross sections $\sigma_{Jn}(v_n)$ from Ref. 12 were used. But the simulations with the model potentials showed that although the exact shape of the inner part of the BO potentials did not influence the spectral structure within the $J''$ groups, it did affect the relative strengths of the groups. This is due to the very poor Franck–Condon overlap of the $X^1\Sigma^+ (v'' = 0, J'')$ initial states and the $A^1\Pi$ component of the scattering wave functions. This overlap depended even on rotation. As a result, the model potentials do not necessarily lead to correct relative strengths of the calculated $\sigma_{Jn}(v_n)$. We thus did not try to precisely determine the rotational distribution.
However, the fitted $p_{J'}$ values for the spectrum taken after 15–30 s storage time indicate a rotational distribution close to room temperature, in agreement with the earlier estimate.26

### 5. Discussion of the model potentials

Table V lists the vibrational indices of the original ab initio potentials,27 together with the vibrational indices of the fitted model potentials, as determined via Eq. (31). The fitted model potentials are shown as dashed curves in Fig. 9. The coefficients of the added polynomials have been fitted such that the X $^1\Sigma^+$ curve is about 3500 cm$^{-1}$ deeper than the $ab$ initio potential, the A $^3\Pi$ state is 500 cm$^{-1}$ shallower, and the a $^2\Pi$ depth had to be reduced by roughly 150 cm$^{-1}$. The fitted value of $\kappa_1$ = 1.3507 in Eq. (29) translates to a depth of 207 cm$^{-1}$ for the long-range c $^3\Sigma^+$ well, compared to 185 cm$^{-1}$ for the original value $\kappa_1$ = 1.94 in Table IV (see Fig. 8).

These model potentials obviously contradict the $ab$ initio potentials, the previous spectroscopic data on the A $^1\Pi$–X $^1\Sigma^+$ system,44 and also the dissociation energy determined in the present work. But this was to be expected given the crude way of forcing the vibrational indices. Since the inner parts are not unique, other ways of adjusting may be possible that stay closer to the $ab$ initio potentials while still yielding the required vibrational indices.

The question of whether the potentials are unique in the long-range part is more difficult to answer. Of course, the value of $C_4$ has a strong, clear influence and could be determined from the spectrum via the Le Roy–Bernstein formula. But since $C_4$ is known exactly, uniqueness rather refers to the $C_6$, $C_8$, and exchange parameters. Before the construction of the long-range analytic form described in Sec. IV D 1, several parameterizations were tried, including the one of Launay and Roueff.47 With their analytical form, tuning the vibrational defects did not lead to an agreement between the measured and calculated spectrum as good as for the final form. On the other hand, we tested if the values of the $C_6$ coefficients derived in this work were essential for the fit: We assumed different signs in Eq. (A4) for the quadrupole-induced dipole contribution to $C_6$, which also implied new $C_8$ coefficients because Eq. (28) was refitted to the $ab$ initio points at long range. With this second set of model potentials, the experimental spectrum could be reproduced almost as well as with the original model potentials, after readjustments of the vibrational indices.

This means that the long-range part of the potentials does affect the spectrum (even if the $v_D$ are kept constant), but that the correct long-range form cannot be uniquely determined from it. In contrast to the $C_4$ term, the $C_6$, $C_8$ and exchange terms influence the spectrum only subtly by changing the couplings via the potential matrix. The resulting effects in the calculated spectrum, although visible, are not systematic enough to deduce the correct values for these parameters.

This ambiguity must be taken into account when comparing the fitted model potentials to the $ab$ initio curves by means of Table V and Fig. 9. A slight change in the long-range form may still be consistent with the $ab$ initio curves (which are not highly accurate at large $r$), but it can nevertheless alter the total vibrational index. With the long-range part thus taking on part of the tuning, the change of the inner part can be less drastic. Actually, the large change required in the inner part to fix the X $^1\Sigma^+$ vibrational defect with the assumed long-range part is a hint that the assumed long-range X $^1\Sigma^+$ curve might not be perfect.

The uncertainty of the vibrational indices in Table V is difficult to estimate. First consider the uncertainty of the vibrational defects, i.e., the fractional parts. Formally, the uncertainties of the potential parameters supplied by the fit can be translated into errors for the vibrational indices. The resulting uncertainties are smaller than 0.001, but these are only meaningful for the particular long-range form assumed in the fit. If the long-range potentials are slightly changed, the optimum vibrational indices may slightly differ from those in Table V. Based on tests, we estimate the defects to be accurate within about $\pm0.05$, regardless of the particular long-range form being assumed.

The integer parts of $v_D$ cannot be directly deduced from the experimental data of this work. But the number of vibrational levels in the model potentials was chosen such that the fitted $v_D$ values were as close as possible to those of the $ab$ initio potentials. The reliability of the integer parts of the $v_D$ values in Table V thus depends on whether the $ab$ initio curves correctly predict the absolute number of vibrational levels. For the A $^1\Pi$, a $^3\Pi$, and c $^3\Sigma^+$ states, Table V shows that the vibrational defects derived from the data differ from the $ab$ initio defects by no more than 0.1 unit, corresponding to the small amount of tuning seen in Fig. 9. Given this accuracy for the defects, the $ab$ initio curves are likely to be correct as to the integer parts of $v_D$.

For the A $^1\Pi$ state, previous spectroscopy also suggests that the number of levels is correct (see Sec. IV C 5). For the shallow c $^3\Sigma^+$ curve, the current work additionally sets $v_D$ = 4.249 as a lower limit because the fifth, fourth, and third highest levels are actually observed (see Sec. IV D 6 below). The number of levels is unlikely to be larger than five, for if a sixth (unobserved) level were to exist further down, the c $^3\Sigma^+$ well would have to be considerably deeper than that achievable with the current analytical long-range form.

The total number of levels remains unclear for the X $^1\Sigma^+$ curve. For the assumed long-range form, the defect of the $ab$ initio potential is too small by about 0.26 (Table V), indicating that the $ab$ initio X $^1\Sigma^+$ state is somehow less reliable. It cannot be excluded that the true X $^1\Sigma^+$ potential has $v_D$ = 23.67 instead of $v_D$ = 24.67.

Because the final model potentials are of no general meaning, but only “effective” in that they reproduce the
spectrum considered here, we do not explicitly give them in numerical form. But equivalent model potentials can be easily constructed, as follows: First compute the long-range part for \( r \gg 2.7 \, \text{\AA} \) as described in Sec. IV D 1 using the data in Table IV. The \( c^{1}\Sigma^+ \) state will then have the correct vibrational index. For the inner parts, the previous potentials\(^{39}\) may be used, smoothly connected to the long-range parts. Finally, vary the depths of the \( X^{1}\Sigma^+ \), \( A^{1}\Pi \), and \( a^{3}\Pi \) wells until a numerical evaluation of Eq. (31) yields the vibrational indices of Table V, or equivalent indices with the same defects.

Although not unique themselves, the model potentials are valuable in that they produce the correct multichannel scattering wave functions at threshold, which are unique (apart from the modulo \( \Pi \) ambiguity of the phases). The model potentials thus have predictive power for the scattering of \( C^+ \) and \( H \), especially for the range of relative kinetic energies \((\lesssim 100 \, \text{cm}^{-1})\) and total angular momenta \((J \approx 9)\) involved in this work. Higher angular momenta in the same energy range will belong to lower vibrational levels, which in turn have shorter-range nuclear wave functions sampling parts of the wells where the model potentials may not be reliable any more. The remainder of our analysis in this paper will rely on these model potentials.

In principle, one could try to construct more meaningful BO potentials by adding the rich, but also fragmentary spectroscopic data on the bound states, as well as some \( ab \) \textit{initio} points to patch those parts where no experimental data is available. Although fitting BO potentials to experimental data is common today, \( CH^+ \) is very challenging in this respect. In order to describe empirically the shape of the inner wells and walls, the parameterization would have to be more flexible than those commonly used for van der Waals molecules, for example, and yet stable enough to handle the missing data. The recent “modified Lennard-Jones” model\(^{14}\) might be used except at long-range where it would have to turn into the complicated long-range part needed for \( CH^+ \).

6. Assignment of resonances

The following spectroscopic analysis is based on the spectrum computed with the model potentials derived from the least-squares fit. In contrast to the fitted spectrum already shown in Fig. 11, the model spectrum used for assignment was generated at higher resolution and not convoluted with the experimental profile. For each upper rotational quantum number \( J' \), the \( e \) and \( f \) parity blocks were separately analyzed. For each feature, we tried to determine the predominant character, i.e., the potential curve on which the resonance would reside in the adiabatic picture (Fig. 2), as well as the corresponding vibrational quantum number. Assignments were accomplished by making small changes to the BO potentials and observing the result in the calculated spectrum, as described in Sec. IV D 3. Although thinking of the multichannel resonances as bound states in the adiabatic potentials is not really appropriate and leads to incorrect predictions as to their exact positions and widths,\(^{12}\) it is quite helpful to understand the structure of the spectrum. As found by Williams and Freed\(^{12}\) and confirmed above by the conventional analysis of the \( A^{1}\Pi \) peaks, most resonances indeed behave like regular rovibrational levels with a fixed rotational constant \( B \).

Figures 12 and 13 show all calculated resonances in the \( e \) and \( f \) parity blocks, respectively. Most of the levels are assigned to one of the curves correlating to the upper fine-structure limit and then grouped into vibrational states.

FIG. 12. Asymptotic energy of all \( e \) resonances in the adjusted theoretical spectrum, as a function of \( J'(J'+1) \). Almost all calculated resonances could be assigned to vibrational levels of the four \( e \) adiabatic curves correlating to the upper fine-structure limit: \( ^1\Pi_1 \) (circles and solid lines), \( ^1\Pi_0 \) (triangles and dotted lines), and \( ^3\Sigma^+ \) (squares and dotted lines). Unassigned peaks are marked with stars. Resonances experimentally detected in this work are represented by full symbols.

FIG. 13. Similar to Fig. 12, but for the \( f \) resonances. Almost all calculated resonances could be assigned to vibrational levels of the four \( f \) adiabatic curves correlating to the upper fine-structure limit: \( ^1\Pi_1 \) (circles and solid lines), \( ^1\Pi_0 \) (triangles and dotted lines), \( ^3\Sigma^+ \) (squares and dotted lines), and \( ^3\Sigma^+ \) (diamonds and dashed lines). Unassigned peaks are marked with stars. Resonances experimentally detected in this work are represented by full symbols.
levels which carry most of the oscillator strength. The spectrum features could be assigned a character in most cases.

For \( J' = 7 \), a few features in Figs. 12 and 13 could not be assigned at all with the procedure used here. This is because the corresponding lower rotations lie below threshold in this case and could not be located with the available scattering code. The use of a multichannel bound state code might have allowed the rotational patterns to be found, but is beyond the current analysis. Furthermore, features at higher \( J' \) are more difficult to assign if they lie within the rotational barrier [Eq. (24)] of the lower fine-structure limit, because then the two adiabatic potentials correlating to that limit in Fig. 2 have to be considered as well.

After the analysis of the theoretical spectrum, we assigned the experimental spectrum by relating the predicted and the observed features. This was easy because of the very good quantitative agreement visible in Fig. 11. All experimentally observed features listed in Table VI have a counterpart in the calculated spectrum, except a few which can be attributed to field-induced dissociation of bound states below threshold. The calculated counterparts to the experimental features could be assigned a character in most cases (Table VI).

On the other hand, only a subset of the predicted features were actually observed in the experiment (those marked with full symbols in Figs. 12 and 13). This does not contradict the experimental data because the missing features are predicted to be too weak to be observed, given the sensitivity of our measurement. Note that even though these levels are not observed, their calculated positions should be no more uncertain than those of the observed peaks, because all features depend on the same vibrational defects, which, in turn, are already determined by the observable features (Sec. IV D 3).

As seen in Figs. 12 and 13, all electronic states that adiabatically correlate to the upper limit contribute to the theoretical spectrum. The observed features most often belong to the \( A^1\Pi \) state \((v' = 11–14)\) and to the \( c^3\Sigma^+ \) state \((v' = 0–2)\) because their features are strong enough to be clearly observed. The strength of the dipole-forbidden \( c^3\Sigma^+ \) levels is clearly due to their accidental proximity to the \( A^1\Pi \) levels which carry most of the oscillator strength. The \( \Pi_1^1 (v' = 12) \) and \( 3\Sigma^+_1 (v' = 1) \) vibrational states in Fig. 12 are so close that they lead to equally strong peaks in the spectrum (see Fig. 11, \( J' = 2 \), at 32 889.6 and 32 892.4 cm\(^{-1}\)). In principle, the two electronic labels are meaningless as a result of strong mixing. It is these two states which are now seen to be responsible for the \( P_1 / R_1 \) and \( P_2 / R_2 \) transitions in Fig. 6, identified but unassigned in the conventional analysis (Sec. IV C 5). Note that, because of different BO potentials, in the original work of Williams and Freed\(^{12}\) the \( a^1\Pi_2 \) resonances lay closest to the \( \Pi_1^1 \) resonances and were the second strongest features. Thus the proximity of a nearly degenerate, dipole-forbidden state is sufficient to permit these dipole forbidden transitions. Note the absence of resonances with \( J' = 0 \) in Figs. 12 and 13. Although the \( X^1\Sigma^+_0^e \), \( c^3\Sigma^+_0^f \), and \( a^1\Pi_0^f \) electronic-rotational states exist for \( J' = 0 \) (Sec. II A), they cannot appear in the present spectrum because the corresponding multichannel wave function lacks the optically pumped \( A^1\Pi \) component, which exists only for \( J' = 1 \).

We do not make an attempt to cast the levels depicted in Figs. 12 and 13 into spectroscopic constants, for several reasons: Apart from the shortcoming of the case (a) labels, such parameterization could hardly include the energy shifts of the resonances caused by the nonadiabatic coupling. Anyway, too few rotational levels appear for some of the vibrational states for such constants to be accurate. Since all resonances follow directly from the model potentials, the vibrational defects (Table V), together with the long-range part of the BO potentials (Table IV) should be regarded as the most compact representation of the spectroscopic data.

V. CONCLUSION

The most important physical results of this work are the new spectroscopic data about the \( \text{CH}^+ \) molecular ion: (1) the new value for the dissociation energy \( D_0 = (32 946.7 \pm 1.1) \) cm\(^{-1}\), and (2) the energies and predissociation widths of dipole-allowed \( A^1\Pi \) levels between the fine-structure levels of the \( \text{C}^+ \) fragment, as observed in the spectrum. These resonances are low rotations \((J' = 1–10)\) of the last bound vibrational levels \((v' = 11–14)\) of the \( A^1\Pi \) electronic state. Furthermore, we have measured (3) the energies and predissociation widths of dipole-forbidden \( a^3\Pi \) and \( c^3\Sigma^+ \) levels between the \( \text{C}^+ \) fine-structure states. These resonances belong to \( a^3\Pi \) \((v' = 17–20)\) and \( c^3\Sigma^+ \) \((v' = 0–2)\). Also, we have presented (4) a revised long-range part for the BO potentials, and determined (5) the vibrational indices of all four BO potentials from constructing model potentials, performing a close-coupling calculation and fitting it to the experimental spectrum. Finally, we have computed from the model potentials (6) the energies and predissociation widths of all low rotational resonances between the \( \text{C}^+ \) fine-structure states.

These spectroscopic data can now be used for several purposes: First, future \textit{ab initio} or empirical potentials of the electronic states correlating to \( \text{C}^+ (3P) + \text{H}(3S) \) may be tested against the data, either via a close-coupling calculation of the spectrum or by comparing only the vibrational indices to those of our model potentials. An accurate \textit{ab initio} study of the long range part \( (r > 2.7 \) Å) would be very interesting, in order to check the analytical description assumed for this region in this work, especially in view of the exchange term which is difficult to describe analytically. Second, the model potentials (which compactly represent the spectroscopic data) may serve for more accurate predictions of the rate coefficients of the interstellar reactions (1) and (2). In case of fine-structure excitation, the currently accepted rate coefficient\(^{12}\) could change because it is sensitive to the long-range part\(^{17}\) where the new model potentials differ significantly from those assumed in Ref. 47. In case of radiative association, the rate coefficient is not likely to differ much from the currently accepted value.\(^{9}\) Although most of the detailed resonant structure of the process can only be predicted for the first time with the present model potentials, the average rate coefficient is mainly determined by the oscillating...
TABLE VI. Peaks in the experimental spectrum (ordered by $J''$ and increasing energy), and assignment according to the close-coupling simulations. Experimental intensities (peak areas) and widths are based on Gaussian fits, and are approximate because most line profiles are not really Gaussian. The experimental resolution is 0.5 cm$^{-1}$. For experimental uncertainties, see Sec. III D. Some experimental peaks were assigned to overlapping resonances belonging to different branches (denoted by extra lines in the table), or to coupled resonances within the same branch (denoted by double character). Peaks corresponding to resonances below the dissociation limit were attributed to field-induced dissociation (FD), and mostly were not assigned.

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tor strengths for the radiative transitions between the initial multichannel scattering wave function and the final bound states. Although slight changes in the potentials may strongly affect individual Franck–Condon factors, the average rate over the numerous final states populated will not depend critically on the shape of the BO potentials.

Apart from the spectroscopic data on CH⁺, there are also more general physical results. The Feshbach resonances in CH⁺ complement those detected earlier in the isovalent molecules SiH⁺ (Ref. 24) and GeH⁺. Confiming these experiments, we find that nonadiabatic coupling between asymptotically degenerate BO potentials can cause strong multichannel effects in the near-threshold photodissociation spectrum. In CH⁺, the multichannel regime is obvious from the “dark” resonances (originating from electronic states other than the pumped A 1Σ⁺ surface) and from the irregular line shapes due to interference of the channel wave functions. Similarly, the SiH⁺ and GeH⁺ spectra showed non-A 1Σ⁺ states, irregularly varying linewidths, and A 1Π features with hyperfine splitting that indicates triplet admixture. Due to the increase of spin–orbit coupling from CH⁺ (63 cm⁻¹) over SiH⁺ (287 cm⁻¹) to GeH⁺ (1767 cm⁻¹), the triplet states become accessible optically, so that Feshbach resonances with triplet character become predominant in GeH⁺, whereas A 1Π levels are the prominent features in CH⁺.

For CH⁺, the close-coupling theory including spin–orbit and rotational coupling provides an excellent fit to the measured spectrum. Similar calculations of selected Feshbach resonances were compared to features measured in SiH⁺ before, but agreed only qualitatively because of the limited accuracy of the BO potentials. Although CH⁺ shows fewer multichannel resonances than SiH⁺ and GeH⁺, it is theoretically the more complicated system, because spin–orbit coupling is about as large as rotational coupling. This ensures, together with the shape of the BO potentials at large r, that the eigenstates of the potential matrix in Eq. (7) vary rapidly with r, and no basis set exists in which the radial equations nearly decouple. In contrast, if spin–orbit coupling is stronger, the eigenstates will be always close to those of the electronic plus spin–orbit Hamiltonian, and rotational coupling can be treated as a perturbation. A single-channel calculation of levels in diagonalized potentials would then be a sufficient approximation. Indeed, equal linewidths found for e and f A 1Π resonances in GeH⁺ indicate that rotational coupling to the X 1Σ⁺ state does not contribute to the predissociation. The complexity of CH⁺ is also due to the fact that, since the fine-structure window is narrower than in SiH⁺ and GeH⁺, the Feshbach resonances lie closer to the upper limit, and thus are closely spaced, long-range vibrational states. In this respect, it is instructive to compare the present photodissociation spectrum also to the one of OH⁺, which we have measured in a similar experiment. In contrast to CH⁺, almost no multichannel effects were seen in OH⁺, although more states are involved and the nonadiabatic couplings are even stronger. The reason is the shape of

<table>
<thead>
<tr>
<th>Experimental data</th>
<th>Assignment</th>
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<tr>
<td>~ (cm⁻¹)</td>
<td>Intensity (arb. units)</td>
<td>Width (cm⁻¹)</td>
</tr>
<tr>
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<td>8</td>
<td>3(1)</td>
</tr>
<tr>
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<td>2</td>
<td>1.1</td>
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<tr>
<td>32 434.0</td>
<td>3</td>
<td>0.4</td>
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<tr>
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the $A^3\Pi$ potential of OH$^+$, which steeply increases with $r$ and suppresses much of the amplitude of the radial wave functions in the coupling region.

Besides these physical results, there are additional, methodical results gained from the successful application of nonstandard experimental and analysis techniques. Regarding the analysis, multichannel effects have been shown to add much spectroscopic information, which is however very hard to extract. The extra features are difficult to assign because they do not follow the usual selection rules, and the irregular line shapes cannot be easily interpreted. Here, we could solve these problems by using as our theoretical model the close-coupling theory adequate for the multichannel regime, by using the BO potentials as free "spectroscopic parameters," and by least-squares fitting not just resonance energies, but the observed cross section itself to make use of the information hidden in the line shapes. This approach proves extremely successful in the sense that the spectrum is fully reproduced by the model and assigned, but there is also a shortcoming. The close-coupling model provides little qualitative insight into the nature of the resonances and their shapes. Trying to explain a spectral feature by studying the underlying multichannel scattering wave functions is possible but very tedious. In principle, tools such as the generalized multichannel quantum defect theory could provide such understanding. In this work, thinking in terms of rotational constants, adiabatic potentials, and perturbation theory, although not strictly valid, has been very helpful.

Obtaining these results would have been impossible without using a new experimental technique. The observation of the multichannel behavior in CH$^+$ required the detection of weak low-$J$ resonances. This required internally cold molecules and an efficient signal detection. The use of a stored molecular ion beam makes both possible. Storage leads to internal cooling of the ions by radiation, and the fast directed fragments can be readily detected. Besides, storage adds a time axis to the spectra. This extra information, which was not used in this work, can in principle help to assign features or to measure lifetimes of excited states. We believe that storing a molecular ion beam for laser spectroscopy is an advantageous extension of the existing techniques.

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APPENDIX: CALCULATION OF $C_6$ COEFFICIENTS

Note: We use SI units throughout this Appendix. The coefficient $C_{6\Lambda}$ in the induction and dispersion expansion of the BO potentials [Eq. (28)] is a sum of several contributions,

$$C_{6\Lambda} = C^\text{iq}_{6\Lambda} + C^\text{id}_{6\Lambda} + C^\text{disp}_{6\Lambda}. \quad \text{(A1)}$$

The first term $C^\text{iq}_{6\Lambda}$ arises from the interaction between the charge of the C$^+$ ion and the induced quadrupole moment of the H atom. It can be calculated exactly from the static quadrupole polarizability of the H atom ($\alpha^q_H = 15 \times 4 \pi \epsilon_0 a_0^5$, Bohr radius). The coefficient is then

$$C^\text{iq}_{6\Lambda} = \frac{e^2}{(4 \pi \epsilon_0)^2} = 7.5 E_h a_0^6,$$ \hspace{1cm} \text{(A2)}

independent of $\Lambda$ ($E_h$, Hartree energy).

The second term $C^\text{id}_{6\Lambda}$ is due to the interaction between the permanent quadrupole moment of the C$^+$ ion and the charge-induced dipole moment of the H atom,

$$C^\text{id}_{6\Lambda} = -\frac{3}{2} e^2 \frac{(\vec{r})_2 p \langle 2 p | \cos \theta \rangle}{(4 \pi \epsilon_0)^2} \times 2 \Lambda (2 \Lambda + 1).$$ \hspace{1cm} \text{(A3)}

In this expression, $\alpha^\text{id}_H = 4.5 \times 4 \pi \epsilon_0 a_0^5$ (Ref. 47) is the static dipole polarizability of hydrogen, and $\vec{r}$ and $\theta$ are the coordinates of the $2p$ electron at the C$^+$ ion, with the internuclear axis taken as the $z$-axis. The mean squared radius of the $2p$ orbital is $\langle \vec{r}^2 \rangle_{2p} = 3.2 a_0^2$. We estimated this value by scaling the radius of maximum radial density of the $2p$ orbital given in Ref. 59. The expectation value $\langle 2 p | \cos \theta \rangle_{2p}$ of the Legendre polynomial $P_2$ is $2/5$ for the $\Lambda = 0$ states and $-1/5$ for the $\Lambda = 1$ states. Inserting these values, we get

$$C^\text{id}_{6\Lambda} = -17.2 E_h a_0^6, \quad C^\text{id}_{6\Lambda} = 8.6 E_h a_0^6,$$ \hspace{1cm} \text{(A4)}

for the $\Sigma$ and $\Pi$ states, respectively.

The leading dispersion term $C^\text{disp}_{6\Lambda}$ was calculated from the expression,

$$C^\text{disp}_{6\Lambda} = \frac{1}{2 \sqrt{2L+1}} \left\{ \epsilon(0,0) - \langle L, 2; \Lambda, 0 | L, \Lambda \rangle \frac{\epsilon(2,0)}{\sqrt{2} \epsilon^2} \right\},$$ \hspace{1cm} \text{(A5)}

which is given in Ref. 51, p. 123, for the case where only one of the atoms has nonvanishing electronic orbital angular momentum $L \neq 0$. In our case ($L = 1$) the Clebsch–Gordan coefficient is $-\sqrt{2}/6$ for $\Lambda = 0$ and $\sqrt{2}/10$ for $\Lambda = 1$. The quantities $\epsilon(0,0)$ and $\epsilon(2,0)$ can be calculated from atomic properties (Ref. 51, p. 125). For $C^2(2p^1; 2P)$ interacting with $H(2S)$, the relevant expressions read

$$\epsilon(0,0) = 2 \sqrt{3} \alpha^\text{id}_H \frac{e^2}{(4 \pi \epsilon_0)^2} \langle \vec{r} \rangle_{2p} \frac{\Delta \epsilon_H}{\Delta \epsilon_H + \Delta \epsilon_c},$$ \hspace{1cm} \text{(A6)}
Here, $\Delta \epsilon_{H}$ and $\Delta \epsilon_{C^+}$ are average excitation energies that can be estimated from the static dipole polarizabilities of the two atoms (Ref. 51, p. 124),

$$\Delta \epsilon_{H} \approx \frac{\hbar}{m_e} \frac{\Delta \epsilon_{C^+} = \frac{\hbar}{m_e}}{\Delta \epsilon_{C^+}}.$$  
(A8)

The static dipole polarizability of C$^+$ is $\alpha_{C^+} = 5.6 \times 4 \pi \epsilon_0 a_0^3$. 61 The reduced matrix element of the quadrupole moment of the C$^+$ ion is 61

$$\langle 2p^1, 2p^2 | Q(2^+)| 2p^1, 2p^2 \rangle = \sqrt{\frac{6}{5}} \langle \tau^2 \rangle_{2p}.$$  
(A9)

Substitution into Eq. (A5) yields

$$C_6^{disp} = 10.6 \ E_h \ a_0^6, \ C_6^{disp} = 6.1 \ E_h \ a_0.$$  
(A10)

According to Eq. (A1), the total $C_6$ coefficients then are

$$C_6 = 0.9 \ E_h \ a_0^6 = 4.3 \times 10^3 \ cm^{-1}, \ \AA^6,$$  
(A11)

$$C_6 = 22.2 \ E_h \ a_0^6 = 1.07 \times 10^5 \ cm^{-1}, \ \AA^6.$$  
(A12)