Vibrational wave packets in the $B^1Π_u$ and $D^1Σ_u^+$ states of Cs$_2$: Determination of improved Cs$_2^+(X)$ and Cs$_2(B)$ spectroscopic constants

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Vibrational wave packets in the $B^1Π_u$ and $D^1Σ_u^+$ excited states of Cs$_2$ have been studied on the $\sim 100$ fs time scale by pump–probe laser spectroscopy. The temporal behavior of the wave packets was monitored by photoionizing the electronically excited molecule with a time-delayed probe pulse and recording the time and energy-integrated photoelectron signal as a function of time delay between the pump and probe pulses. For the $B^1Σ_u^+$ experiments, wave packets were produced by exciting the $B^1Σ_u^+ \rightarrow X^1Σ_g^+$ transition in the $\sim 740–790$ nm region and subsequently detected by photoionizing the molecule at wavelengths between 565 nm and 600 nm. By simulating the experimentally observed transients with the density matrix formalism (and explicitly accounting for laser chirp and $|Δν| > 1$ coherences), improved values for the equilibrium internuclear separation for the Cs$_2(B^1Π_u)$ state and $T_e$ for the Cs$_2(X)$ state were determined to be $R_e(B^1Π_u) = 4.93 ± 0.03$ Å and $T_e(Cs_2^+(X)) = 29.930 ± 100$ cm$^{-1}$, respectively. Similar experiments were conducted for the $D^1Σ_u^+$ state. Wave packets composed of vibrational levels ($v' \approx 40–50$) perturbed by the bound $3^1Π_u^− \rightarrow X^1Σ_g^+$ potential surface by driving the $D^1Σ_u^+$ transition in the 575–610 nm spectral interval.

I. INTRODUCTION

The temporal dynamics of vibrational wave packets have been studied in several diatomic molecules, including the alkali dimers (Li$_2$, Na$_2$, ..., Cs$_2$),$^{1–10}$ NaI,$^11$ and I$_2$.$^{12,13}$ Since the production of a wave packet entails the coherent excitation of two or more states, generating a vibrational wave packet with a single optical pulse requires that the bandwidth of that pulse exceed the local vibrational state separation ($≈ ω_e ∼ 2v ω_{a,Δv}$) for the electronic state under study. Experiments to date have been confined to diatomics for which the vibrational frequency $ω_e < 200$ cm$^{-1}$ and have generally involved detecting wave packet motion by combining photoionization of the molecule with time-of-flight photoelectron energy or ion mass spectrometry analysis.

Recently, vibrational wave packets in the $C^1Π_u$ state of Cs$_2$ were produced and examined by laser pump–probe spectroscopy experiments in which the temporal history of the wave packet was recorded by monitoring the time and energy-integrated photoelectron current.$^{3,4}$ Because of the large difference between the equilibrium internuclear separations for the Cs$_2(C)$ state and the ground state of the dimer ion ($R_0(Cs_2^+(X))−R_0C=0.75$ Å), the $C^1Π_u$ state is photoionized in a narrow Franck–Condon region located near the classical inner turning points for the Cs$_2^+(X, ν' \approx 65–90)$ vibrational levels. Consequently, wave packets in the Cs$_2(C^1Π_u)$ state give rise to a photoelectron current that is deeply modulated as the time delay ($Δt$) between the pump and probe pulses is varied. Since this approach to wave packet detection does not rely on resolving electron or ion energies, the photoelectron signal is expected$^4$ to exhibit significant modulation only if the potential surfaces of the intermediate and final (ion) molecular states differ appreciably.

In this paper, similar experiments are reported for the $B^1Π_u$ and $D^1Σ_u^+$ states of Cs$_2$. Two color pump–probe experiments for the $B^1Π_u$ state entailed exciting the molecule in the $740–790$ nm region and photoionizing the $B$ state at wavelengths between 565 nm and 600 nm. For the $D^1Σ_u^+$ experiments, the pump wavelength was varied over a $35$ nm interval (575–610 nm) whereas the central probe wavelength was fixed at 750 nm. Comparison of the experimental data with wave packet transients calculated from the density matrix formalism$^5$ yields improved values for the equilibrium internuclear separation for the $B^1Π_u$ state and $T_e$ for the Cs$_2^+$ ion ground state.

The $B$ and $D$ states of Cs$_2$ are interesting for wave packet experiments for several reasons. In contrast to Cs$_2(C^1Π_u)$, for example, the value of $R_e$ for the $B^1Π_u$ state differs from that for Cs$_2^+(X)$ by $<0.4$ Å.$^{4,16,17}$ Thus, the $B$ state provides an interesting test of the extent of applicability of the photoelectron current wave packet detection technique. The $D^1Σ_u^+$ state was first characterized comparatively recently (1982).$^{18,19}$ is known to have an equilibrium internuclear separation intermediate to those for the ground states of the dimer and dimer ion, and $R_{e,D}−R_{e,X}≈1$ Å. Consequently, producing and detecting $D$ state wave packets is complicated by small $D−X$ Franck–Condon factors (FCFs). Furthermore, photoexcitation of $D^1Σ_u^+$ from ground at $\sim 580–600$ nm populates the $ν' \approx 40–50$ vibrational states that are known from high resolution laser spectroscopic experiments$^{20–23}$ to be strongly perturbed by the bound $2^1Π_{1u}$ state.
et al. have recently reported producing wave packets in the Cs$_2$(B) state in single color pump–probe experiments at 768 nm. Because of the pump wavelength and cooling of the dimers in a supersonic expansion, the B($v' = 0, 1$) states were the dominant contributors to the wave packet composition. The experiments described here involve a Cs$_2$ ground state population that is thermalized at 260–300 °C, which results in wave packets on the intermediate potential surface (B $^1\Pi_u$ or D $^1\Sigma_u^-$) comprising at least 15–20 vibrational states. Although such wave packets dephase more quickly than do their counterparts consisting of only a few vibrational levels, combining the density matrix formalism with data acquired by varying experimental parameters (the pump and probe wavelengths, in particular) allows one to isolate key spectroscopic constants of the intermediate and final electronic states.

II. EXPERIMENT

The experimental arrangement and data acquisition techniques are similar to those described in detail previously and will only be reviewed here. Briefly, pulses having temporal widths (sech$^2$) of 80–100 fs and energies of ~300 µJ are produced at 30 Hz by a colliding pulse mode-locked (CPM) oscillator and a four stage dye amplifier system driven by a frequency-doubled Nd:YAG laser. Supercontinua are produced by focusing the pulses into water and, after dividing each pulse into two with a beamsplitter, one is time-delayed with respect to the other by a retroreflector mounted onto a computer-controlled translation stage. Interference filters remove ~10 nm (FWHM) spectral segments from each pulse and both are focused into a heat pipe containing Cs vapor at pressures ranging from 10 to 100 Torr (1.5×10$^{17}$≤[Cs]≤1.2×10$^{18}$ cm$^{-3}$). A cylindrical diode (proportional counter) installed in the heatpipe allows for the time and energy-integrated photoelectron current to be measured. Care must be taken to ensure that the proportional counter is not saturated.

III. RESULTS AND DISCUSSION

A. Temporal domain data

Experiments were carried out for several values of the central pump wavelength ($\lambda_1$) while the probe wavelength ($\lambda_2$) and Cs number density in the heat pipe were held constant. Representative results for vibrational wave packets produced in the Cs$_2$(B $^1\Pi_u$) state are presented in Fig. 1 which shows the variation of the total photoelectron current with $\Delta t$. Three traces obtained for $\lambda_1 =$ 758 nm and $\lambda_2 =$ 600 nm are shown to illustrate the reproducibility of the experiment and the baselines for the traces have been intentionally offset for clarity. The heatpipe temperature was fixed at 573 K.

For pump wavelengths (\(\lambda_1\)) beyond ~765 nm, signal quality degraded and wave packet dephasing accelerated. This is to be expected for two reasons. As a result of the B–X FCFs and the concomitant B–X absorption spectrum (cf. Fig. 3), a substantial fraction of the B state population produced by the pump pulse resides in $v' \geq 20$ states. As an example, Fig. 4 illustrates the vibrational distribution of the Cs$_2$(B) and Cs$_2$(X) populations for $T$ ≤ $\lambda_1$ ≤ 763 nm.
$=573$ K, calculated from the $\text{Cs}_2$ ($X$ and $B$) and $\text{Cs}_2^+$ ($X$) spectroscopic constants to be discussed in Sec. III B 1, and the measured pump and probe spectra. Second, the anharmonic constant $\omega_{Xe}$ for the $B^1\Pi_u$ state is $\sim 0.08$ cm$^{-1}$ (cf. Dunham coefficients of Ref. 16) which is roughly a factor of 2 larger than that for the $C^1\Pi_u$ state ($\omega_{Xe}=0.042$ cm$^{-1}$). Since wave packet dephasing is dependent on both the anharmonic constant for the state under study and the number of vibrational levels in the excited state ensemble from which the wave packets are produced, one would expect the greater anharmonicity of the $B^1\Pi_u$ state to lead to faster dephasing of the wave packet. This is consistent with our observation of $B$ state wave packet dephasing in $\sim 6$ ps, in contrast to wave packets produced in the $C$ state which have been shown$^{3,4}$ to dephase in 10–15 ps.

The data of Figs. 1 and 2 differ from those of Refs. 5 and 6 in two respects. Because the wave packets in the experiments of Blanchet and co-workers were composed primarily of the $B(v'=0,1)$ vibrational wave functions (due to cooling of $\text{Cs}_2$ in a supersonic expansion and the $B-X$ FCFs), they dephased slowly and oscillations in the $\text{Cs}_2^+$ ion signal owing to motion of the $B$ state wave packet persist for tens of ps. In the present experiments, significant contributions from more than 20 $B$ state vibrational levels result in much quicker dephasing of the wave packet, although excited state vibrational levels higher than those accessed in Refs. 5 and 6 are populated and probed. Also, the tunability of the pump ($\lambda_1$) and photoionization ($\lambda_2$) pulses permits one to observe the wavelength dependence of the temporal and spectral characteristics of the wave packet transients, in addition to optimizing the $\text{Cs}_2(B,v')$ ionization probability. Previous experiments$^4$ examining the $C^1\Pi_u$ state of $\text{Cs}_2$ have shown the latter to be a key factor in determining the detectability of the wave packet.

Photoionization data similar to those of Fig. 2 but for rovibrational wave packets generated in the $D^1\Sigma_u^+$ state of $\text{Cs}_2$ are illustrated in Fig. 5. For these experiments, the central probe wavelength ($\lambda_2$) was fixed at 750 nm (with a 25 nm FWHM bandpass filter) while $\lambda_1$ was varied over the 575–610 nm region. For $\Delta t<0$, no signal is generally detected (as one expects since the probe precedes the pump), except when the pump wavelength is also suitable for photoionizing the $B$ state. In such a case ($\lambda_1=600$ nm, $\lambda_2=750$ nm, for example, cf. Fig. 2), $B$ state wave packets are observed for $\Delta t<0$ and $D$ state wave packets when $\Delta t>0$. Because of the FCFs for the $D-X$ transition of $\text{Cs}_2$ (to be addressed in Sec. III C), $D-X$ absorption is approximately two orders of magnitude weaker than that for the $C-X$ transition. Note that the periodicity of the signals in Fig. 5 is $\sim 2$
ps which implies an average, local vibrational state energy spacing in the $D^1\Sigma_u^+$ state of 16.7 cm$^{-1}$, corresponding to $\Delta G$ in the vicinity of $v' = 36$. However, as will be discussed later, the $D-X$ FCFs favor transitions to $D(v' = 40-50)$, vibrational levels whose positions have been shown to be perturbed through the interaction of $D^1\Sigma_u^+$ with the bound $2^3\Pi_{oa}$ state. The latter is correlated, in the separated atom limit, with $\text{Cs}(5d^2D_{3/2}) + \text{Cs}(6s^2S_{1/2})$ (Ref. 22) and shifts the $35 \leq v' \leq 58$ states by as much as 0.7 cm$^{-1}$ (Ref. 22). From rotational linewidth measurements, Kato et al. inferred the predissociation rates for the $D^1\Sigma_u^+ (v' = 46, J' = 30-70)$ states to be $10^9$ s$^{-1}$. In light of these comments, it is interesting to note that dephasing of the wave packets in Fig. 5 occurs more slowly ($\sim 7-9$ ps) than is observed for the $B$ state experiments, a result that is partially attributable to the fact that $\omega_c\chi_c(D) < \omega_c\chi_c(B)$. The irregularity of the $D$ state rovibrational spacing in this region might otherwise be expected to lead to more rapid dephasing of the wave packet than that characteristic of the $B$ state.

### B. Analysis of $B^1\Pi_u$ wave packets

#### 1. Density matrix theory

Numerical calculations of the temporal behavior of vibrational wave packets in the $B$ (and $D$) states have been carried out according to the density matrix approach described in Ref. 15 and applied in Ref. 4 to the $\text{Cs}_2(C^1\Pi_u)$ state. The potential adopted for the $X^1\Sigma_g^+$ state was generated by the IPA (inverted perturbation approach) based on the eigenenergies, measured by Weickenmeier et al., for the lowest 138 vibrational levels. The $B^1\Pi_u$ vibrational eigenenergies, which have been measured up to $v' = 50$ by Doppler-free polarization spectroscopy, were extrapolated to $v' = 50$ by a polynomial (Dunham-type) expansion, where $G(v' = 50) = 1520$ cm$^{-1}$, which is still well below the $B$ state dissociation energy ($\sim 2338$ cm$^{-1}$). The $B^1\Pi_u$ potential was then constructed by the IPA.

Turning now to the final state for the wave packet production and detection sequence $[\text{Cs}_2(X^2\Sigma_g^+)]$, a source of uncertainty in the calculations is the absence in the literature of measured spectroscopic constants for the dimer ion ground state. Pseudopotential and effective core potential calculations for $\text{Cs}_2^+(X)$ predict $R_e(X) = 5.25 \pm 0.05 \text{ Å}$ and $\omega_c = 34.3 \pm 3$ cm$^{-1}$ (Ref. 17, 28-30) but recent simulations by Braun et al. of the $C^1\Pi_u$ wave packet experiments of Ref. 3 suggest revising $R_e(\text{Cs}_2^+(X))$ down by 6% to 4.97 Å. Since the $\text{Cs}_2^+(X^2\Sigma_g^+)$ state is not well-characterized, in all of the calculations to follow its potential is approximated by a Morse potential for which the larger value for $R_e (5.25 \text{ Å})$ was adopted and the vibrational frequency was taken to be $34$ cm$^{-1}$. On the basis of several theoretical values and an experimental lower limit, $D_e$ for the dimer ion ground state is initially taken to be $5060 \pm 800$ cm$^{-1}$, which yields $T_e(\text{Cs}_2^+(X)) = 30,000 \pm 800$ cm$^{-1}$ if the dissociation energy for the neutral dimer ground state ($X^1\Sigma_g^+$) is assumed to be $D_e = 3649.5$ cm$^{-1}$. It is not expected that the description of the $\text{Cs}_2^+(X)$ state by a Morse potential introduces significant error into the calculations because the FCFs for the ionization of the $B^1\Pi_u$ state $[\text{Cs}_2^+(X) \rightarrow \text{Cs}_2^+(B)]$ strongly favor transitions terminating on the lowest vibrational levels of the $X^2\Sigma_g^+$ state (cf. Fig. 4).

Rotationless wave functions for the $\text{Cs}_2X$ and $B$ states as well as the ground state of $\text{Cs}_2^+$ were calculated by the Numerov method. FCFs for the $\text{Cs}_2(B \rightarrow X)$ and $\text{Cs}_2^+(X) \rightarrow \text{Cs}_2^+(B)$ transitions were then computed. From the measured pump and probe laser spectra, the calculated FCFs, and an assumed Boltzmann distribution for the $\text{Cs}_2$ ground state population, the experimentally determined photoelectron current-time delay ($\Delta t$) scans were simulated by the density matrix technique proposed by Gruebele and Zewail. Since the ionization signal reflects the probability of finding a molecule in the final $[\text{Cs}_2^+(X)]$ state for a given value of $\Delta t$, the wave packet transient can be expressed as the sum of vibrational and rotational terms:

$$I(\Delta t) \propto \sum_{v_1', v_2' < v_1'} \frac{2}{1 + b_{12}(\Delta t)^2} \left[ \cos(2\pi c \Delta t \cdot \Delta G_{12}) + b_{12} \Delta t \sin(2\pi c \Delta t \cdot \Delta G_{12}) \right]$$

$$+ \frac{1}{2} \sum_{v_1', v_2'} \left( 1 - b_{12}^2(\Delta t)^2 \right) \cos(2\pi c \Delta t \cdot \Delta G_{12}) e^{-b_{12}^2(\Delta t)^2}$$

$$\times \sum_v F(v'_{1}, v') F(v'_{2}, v) E_p(\omega_{v'} - \omega_{v}) E_p(\omega_{v} - \omega_{v}) \sum_v F(v_{1}, v) F(v_{2}, v) E_L(\omega_{v_{1}} - \omega_{v}) E_L(\omega_{v_{2}} - \omega_{v}) e^{-E_v/kT},$$

where

$$v, v', v_1'$$

and $v_2'$ represent $\text{Cs}_2$ ground ($X^1\Sigma_g^+$), intermediate ($B^1\Pi_u$ or $D^1\Sigma_u^+$), and ion $[\text{Cs}_2^+(X)]$ vibrational states, respectively. $B_e$ is the $X^1\Sigma_g^+$ rotational constant, while $B_e'$ and $\alpha_e'$ are rotational constants for the intermediate state, $16,22,23$

$$F(v_{1}, v)$$

is the FCF associated with the transition between the indicated vibrational and electronic states, $E_L(\omega)$ and

$$kT,$$
$E_p(\omega)$ are the pump and probe laser spectra, respectively, $\Delta G_{12}=E(v_1',J'=0)-E(v_2',J'=0)$ is the difference in the energies of the two intermediate state vibrational levels $v_1'$ and $v_2'$, and $E_u$ (which appears in the Boltzmann term) is the energy of the $X^1\Sigma_g^+$ ($v,J=0$) level. Although Eq. (1) does not explicitly sum over all $J$, it is valid for the experiments reported here because the ground state rotational temperature ($\approx$ vapor temperature) allows for the sum over $J$ to be approximated as an integral. One simplification, however, that was not made in these calculations was to restrict $v_1' - v_2'$ to be solely $\pm 1$. The bandwidth of the amplified CPM laser pulses compels us to consider higher order coherences ($\pm 2$, $\pm 3$, ...).

The rotational transient, described by the first two terms of Eq. (1), is expressed in terms of a sinusoid of frequency $\omega_1$, and a rotational dephasing time, $b_{rot}^{-1}$, which is $\approx 21$ ps (considering only $\Delta v'=\pm 1$ coherences) for the $B^1\Pi_u$ state of Cs$_2$. For the $B$ state experiments reported here, however, a key factor in determining the wave packet dephasing time is the anharmonic coefficient $\omega_{x'' \ell}$ which causes dephasing on the time scale of $t_d= (4\omega_{x'' \ell}^2 \cdot n \cdot c)^{-1}$, where $n$ is the number of $B^1\Pi_u$ state vibrational levels composing the wave packet. For $n=15$ (cf. Fig. 4), $t_d\approx 7$ ps which is consistent with experimental observations.

The term in Eq. (1) involving $b_{rot}$ constitutes the rotational transient that dephases on a time scale of $b_{rot}^{-1} \approx 1.4$ ps. Because of its small magnitude, the rotational transient has the primary effect of increasing the amplitude of the first two oscillations in the photoelectron current versus $\Delta t$ data scans (Figs. 1, 2, and 5).

For experimental situations in which the laser chirp cannot be neglected (i.e., the change in phase over the laser bandwidth is $\approx \pi$), it can be explicitly incorporated into Eq. (1) by adding

$$\Delta \theta = \theta(v, v_1') - \theta(v, v_2') + \theta(v_1', v'') - \theta(v_2', v'') \quad (4)$$

where $\theta(v_a, v_b)$ is the spectral phase of the pump or probe laser pulse at the frequency corresponding to the energy difference between $v_a$ and $v_b$. When the chirp is linear, for example, this phase factor will be proportional to $(\omega_{v_1'} - \omega_{v_2'}) = \omega_0^2$, where $\omega_0$ is the center frequency of the laser pulse. Unfortunately, accounting for chirp in the calculations complicates the separation of the four-dimensional sum over $v_1'$, $v''$, $v_2'$, and $v''$ into sets of lower-order sums as indicated in Eq. (1). The result is a drastic increase in computational time.

2. Comparison of theory with experiment

Simulating the experimentally observed $B^1\Pi_u$ vibrational transients with the density matrix formalism offers the opportunity to isolate particular Cs$_2$ spectroscopic constants. In particular, optimizing the fit between simulations and experimental data with respect to specific temporal and spectral characteristics of the transient allows for the values for the $B$ state equilibrium internuclear separation ($R_e$) and $T_e$ for the Cs$_2$ ground state to be improved.

One characteristic or observable of the Cs$_2$ ($B$ and $D$) wave packet transient that serves as a test of the theoretical predictions is the transient’s modulation depth. Somewhat arbitrarily defined as the difference between the magnitude of the photoelectron current peak at $\Delta t=0$ and the first local minimum in the signal, the modulation depth is a rapidly varying function of the central pump wavelength $\lambda_1$. An examination of Fig. 2 suggests, and the open circles (○) of Fig. 6 confirm, that the modulation depth of the Cs$_2$($B^1\Pi_u$) transients peaks for $\lambda_1 \approx 751$ nm when the probe wavelength ($\lambda_2$) is fixed at 600 nm. In contrast, numerical simulations of the vibrational-rotational transient, based on the density matrix model and spectroscopic constants of Sec. III B 1, show quite different behavior, predicting that the maximum modulation depth of the transients will be observed at longer wavelengths ($\lambda_1 \approx 760$ nm).

As one might expect, the calculated modulation depth is found to be relatively insensitive to the Cs$_2^+$ spectroscopic constants. Varying the Cs$_2^+$($X$) spectroscopic constants $\omega_x$ and $R_e$ by more than one standard deviation (σ) results in only a negligible change in the value of $\chi^2$ describing the fit of the theoretical transient to the experimental data. Specifically, $\Delta \chi^2 \approx 3\%$ per $\pm \sigma$. Furthermore, a sensitivity analysis with respect to $T_e$[Cs$_2^+$($X$)] shows the assumed value (3 x 10$^{13}$ cm$^{-1}$) to actually yield the best fit (i.e., minimum $\chi^2$) between theory and experiment.

All of the remaining constants required by the calculations have been measured, directly or indirectly, by laser spectroscopy, and the ground state constants (Dunham coefficients) have been determined to high precision. Despite the excellent experiments by Diemer et al., however, the $B^1\Pi_u$ constants are not known to the same degree of precision. The equilibrium internuclear separation ($R_e$), for example, was determined in Ref. 16 by constructing the $B^1\Pi_u$ potential from the Dunham coefficients by the RRK and IPA methods and, subsequently, calculating the rotational con-
constants $B_u$ from the vibrational wave functions for the state. In this way, $R_e$ was estimated to be 4.85 Å. Utilizing a relativistic effective core potential, Jeung et al. calculated $R_e(B)$ to be 4.86 Å.

Simulations show that the quality of the fit between the theoretical and experimental $B$ state transients is quite sensitive to the assumed value of $R_e$. Consider, for example, Fig. 7. Vibrational transients were calculated for 17 values of $R_e(B)$ ranging from 4.83 Å to 5.0 Å and six values of $\lambda_1$ ($747 \pm \lambda_1 \approx 771$ nm, with $\lambda_2$ held constant at 600 nm). For a given value of $R_e$, the modulation depth associated with each theoretical transient was compared with the experimental result and $\chi^2$ was then calculated by summing the squares of the differences between theory and experiment over all six $\lambda_1$ studied for that value of $R_e$. That is, $\chi^2 = \Sigma(d_{\text{exp}} - d_{\text{theory}})^2 / \sigma_{\text{exp}}^2$, where $d$ represents the modulation depth for a specific transient. As illustrated by the open circles of Fig. 7, increasing $R_e$ from 4.85 Å results in a rapid drop in $\chi^2$ and $\chi^2/(N-2)$ [where N=6] < 1 for 4.91 $\leq R_e(B) \leq 4.96$ Å. An uncertainty for the value of $R_e$ presented in Ref. 16 was not given and, on the basis of extensive comparisons of experiment with theory, it is proposed here that a more precise value for the $B \, ^1Π_u^+$ equilibrium internuclear separation is $4.93 \pm 0.03$ Å. Returning now to Fig. 6, the solid dots depict the dependence of the calculated modulation depth on $\lambda_1$ if $R_e = 4.93$ Å. As a check on this revised value, the variation of $\chi^2$ with changes in the $\text{Cs}_2^+ (X)$ constants was revisited, now assuming $R_e(B \, ^1Π_u^+)$ to be 4.93 Å. As before, the fluctuations in $\chi^2$ were found to be negligible for variations exceeding $\pm 3\sigma$ in either $\omega_e$ or $R_e$. A key result of this work, then, is that ultrafast experiments conducted in the temporal domain are able, by varying the pump and probe spectra and computational analysis of the resulting rovibrational transients, to determine molecular spectroscopic constants or, potentially, improve upon those measured in the frequency domain.

Further confirmation for the increase in $R_e(B)$ proposed above is provided by an examination of the frequency composition of the experimental and calculated wave packet transients. Fourier transform (or Maximum Entropy Method, MEM) frequency spectra of the experimental data of Fig. 2, for example, show a dominant peak at 31.4 $\pm 0.8$ cm$^{-1}$ for $\lambda_1 \approx 751$ nm and $\lambda_2 \approx 600$ nm, where the uncertainty represents one standard deviation. When $\lambda_1$ is increased to 768 nm (with $\lambda_2$ held fixed at 600 nm), the peak response in the frequency spectrum shifts to 33.8 cm$^{-1}$. These results are to be expected because $\omega_u(B \, ^1Π_u^+) = 34.3$ cm$^{-1}$ (Ref. 16) and 31.4 cm$^{-1}$ corresponds to the $\Delta G$ value for the $B$ state in the vicinity of $\nu' = 18$, which is approximately $\langle \nu' \rangle (\approx 16)$ for the $B \, ^1Π_u^+$ population distribution produced by the pump ($\lambda_1 = 751$ nm, cf. Fig. 4). As $\lambda_1$ is increased, however, the $B-X$ FCFs favor excitation of lower-lying $B$ state vibrational levels ($\langle \nu' \rangle \approx 14$ and 12 for $\lambda_1 = 756$ and 763 nm, respectively) and, hence, the $\Delta G$ value reflected in the wave packet motion rises.

In an effort to evaluate from a different perspective the value of $R_e(B \, ^1Π_u^+)$ presented earlier, the frequency spectra of 20 wave packet transients, acquired experimentally for various values of $\lambda_1$, $\lambda_2$, and temperature, were calculated. For each transient, the experimentally determined fundamental frequency was compared with that resulting from the simulations and the results are displayed in Fig. 7 by the solid circles. In this case, $\chi^2$ for the observable (wave packet fundamental frequency) exhibits a broad minimum in $R_e$ and falls below one for $R_e \approx 4.86$ Å. This result provides further support for the conclusion that $R_e(B \, ^1Π_u^+)$ is slightly larger than the value estimated in Ref. 16.

A similar process was then used to re-evaluate the $\text{Cs}_2^+$ ground state constants. Taking $R_e(B)$ now to be 4.93 Å, the $\text{Cs}_2^+$ spectroscopic constants ($\omega_e$, $R_e$, and $T_e$) were altered from the values of Sec. III B 1 and, as shown in Fig. 8, the most striking results were obtained for $T_e$. The experimental data from which these results were calculated were those described earlier in connection with the study of the modu-
lution depth (six sets: various $\lambda_1$, $\lambda_2 = 600$ nm, $T = 533$ K) and vibrational frequency (20 sets: various $\lambda_1$, $\lambda_2$, and $T$) of the transients. Two curves are given in Fig. 8, both of which illustrate the dependence of $\chi_2^\ell$ on the assumed value of $T_e$ for the $\text{Cs}_2^+$ ground state. The open circles represent $\chi_2^N/(N - 2)$ associated with the modulation depths of the simulated and experimental wavepacket transients. As noted earlier, $\chi_2^N$ for this particular observable takes on its minimum value in the vicinity of the value of $T_e$ (30 000 cm$^{-1}$) adopted originally in the model and denoted by the vertical arrow. For $29 900 \leq T_e \leq 30 100$ cm$^{-1}$, $\chi^N$ is essentially flat but increases rapidly for values of $T_e$ below $\sim 29 850$ cm$^{-1}$. In particular, $\chi^N$ rises above one for $T_e \approx 29 830$ cm$^{-1}$ (indicated by the left dashed vertical line in Fig. 8). When monitoring the (fundamental) vibrational frequency of the wavepacket data (denoted in Fig. 8 by the solid dots), however, $\chi^N$ changes relatively slowly until $T_e$ is increased beyond 30 000 cm$^{-1}$. At $\sim 30 300$ cm$^{-1}$ (indicated by the second dashed vertical line, at right), $\chi^N$ surpasses one and rises rapidly. On the basis of these results, we propose the revised value of $29 930 \pm 100$ cm$^{-1}$ for $T_e$ of $\text{Cs}_2^+$($X^2\Sigma^+_1$), for which the lower limit of the constant is defined by the modulation depth data of Fig. 8 while the upper limit is set by the comparison between the vibrational frequencies of the experimental and theoretical wavepacket data. Revising $T_e$ also implies that $D_u[\text{Cs}_2^+(X)]$ is now $5130 \pm 100$ cm$^{-1}$ which is in agreement with the lower limit of 0.59 $\pm$ 0.06 eV established by Helm and Möller from photodissociation experiments.

This suggested value for $T_e$ is only slightly smaller than the value originally adopted for the computer model but the comparison between simulation and experiment has permitted the estimated uncertainty in the constant to be reduced considerably. However, it should also be mentioned that $T_e[\text{Cs}_2^+(X)] = 29 930$ cm$^{-1}$ as proposed here is considerably larger than calculations would suggest (29 200–29 400 cm$^{-1}$). Finally, analyses similar to that of Fig. 8 for $\omega_2^\ell$ and $R_e$ of the $\text{Cs}_2^+$ ground state yield weak variations in $\chi^\ell$ (i.e., $\Delta \chi^\ell$ changes by $< \pm 10\%$ per $\sigma$) when either constant is altered from its assumed value ($\omega_2 = 34$ cm$^{-1}$ and $R_e = 5.25$ Å).

Before leaving this section, the potential contribution of higher-order coherences (interactions between nonadjacent vibrational levels) and laser chirp to $B$ state wave packet data (e.g., Figs. 1 and 2) should be considered. Figures 9 and 10 show the results of simulating wave packet transients produced by pump wavelengths of 751 nm and 762 nm and $\lambda_2 = 600$ and 580 nm, respectively. For both experimental scans (photocurrent as a function of $\Delta t$), three simulations are given. The first [part (b)] of Figs. 9 and 10 includes both $\Delta v = \pm 1$ coherences and the chirp of the pump and probe pulses. Specifically, based on spectral and cross-correlation measurements, a linear positive chirp, corresponding to the broadening of nearly transform-limited pump and probe pulses to $\sim 180$ fs at the heatpipe, was incorporated into the simulations. Doing so improves the fit of all of the calculated transients to the data. If higher-order ($|\Delta v| > 1$) coherences are now also incorporated into the calculations, trace (c) results. The beneficial impact of accounting for the known laser pulse chirp is clear from panel (d) of Fig. 9 which illustrates the transient calculated when $|\Delta v| \geq 1$ coherences are incorporated into the calculations but chirp is neglected. A similar comparison between experiment and simulations is presented in Fig. 10 for $\lambda_1 = 762$ nm and $\lambda_2 = 580$ nm. MEM frequency spectra of the eight wave packet transients of Figs. 9 and 10 are shown in Fig. 11. Comparing the three figures, it is obvious that higher-order coherences manifest themselves in the frequency domain as harmonics of the fundamental vibrational frequency. In the temporal domain, however, the $|\Delta v| > 1$ coherences have the effect of narrowing the peaks in the transients [cf. panel (d) of Figs. 9 and 10], a result that is at odds with experiment. Accounting for the chirp of the pump and probe laser pulses ameliorates both of these effects. For all of the data obtained to date, the amplitude of the $\Delta v = 2$ peak in the frequency domain, for example, is consistently $\leq 5\%$ of that for the fundamental. As illustrated in parts (d) and (h) of Fig. 11, the simulations are unable to account for this fact if the chirp of the laser pulse is ignored. If, however, the linear chirp is now imposed onto the pump and probe pulses, the amplitudes of the second
(Δν = 2) and higher harmonic frequency components are suppressed with respect to the fundamental [Fig. 11(c) and (g)].

The fact that including a positive linear chirp into the wave packet simulations is necessary to explain the data is gratifying since normal dispersion (n′′(λ) > 0) in conventional optical elements produces positive chirp at the leading edge of a transform-limited pulse. Furthermore, self-phase modulation, the driving mechanism of continuum generation, produces a nonlinear chirp that can be approximated as a positive linear chirp. It is interesting to note that if the sign of the chirp is reversed, the simulated transients are more narrow than those resulting from not considering chirp at all.

Therefore, improvement in the simulation of experiments is achieved by incorporating |Δν| > 1 coherences and laser chirp into the calculations and, to our knowledge, these are the first simulations to do so. Considering higher-order contributions to the laser chirp may well improve further the agreement between theory and experiment. However, the gains are modest and, in the absence of detailed measurements of laser pulse phase, most aspects of the wave packet transient’s frequency and temporal characteristics are described adequately by including only Δν = ±1 coherences.

C. Wave packets in the D 1Σ+ state

The D 1Σ+ state of Cs has been studied extensively by several high resolution laser spectroscopic techniques, including Fourier transform spectroscopy and Doppler-free polarization spectroscopy. As noted earlier, D 1Σ+ vibrational levels above v′ = 30 are perturbed by the bound 2 3Πu state and energy shifts exceeding 0.1 cm⁻¹ were measured by Kato et al. for 14 D 1Σ+ vibrational states in the 30 ≤ v′ ≤ 58 interval. Predissociation of D 1Σ+ also occurs through two mechanisms: spin-orbit interaction with 2 3Πu, and L-uncoupling between the 2 3Πu state and the repulsive c 3Σv⁺ potential.

In calculating the D−X FCFs shown in the upper portion of Fig. 12, the X state potential generated from the IPA data of Ref. 18 and the D 1Σ+ state RKR potential of Ref. 22 (for v′ = 58) as well as the v′ = 59–65 state energies of Ref. 23 were used. For higher vibrational states, the D state potential was approximated by the Morse function. The lower half of Fig. 12 displays the D−X absorption spectrum, calculated by weighting the FCFs with the X state vibrational state population distribution at T = 600 K. Because of the large difference between Rg for the ground and D states (∆Rg = Rg,D [5.71 Å, Ref. 22] − Rg,X [4.65 Å, Refs. 18,27] = 1 Å), maximum absorption occurs in the 570–580 nm region which arises predominantly from transitions to v′ ≈ 30–50 states. A comparison of the experimental photoelectron current-Δt scans for λ1 = 577 nm and 600 nm with the results of numerical calculations are illustrated in Fig. 13. For vibrational wave packets composed of lower-lying D state vibrational levels, the simulations match the data reasonably well. When λ1 = 600 nm, for example, D−X transitions populate predominantly v′ ≈ 10–20 states which are well-characterized and essentially free of perturbations. Near the peak of the D−X absorption band (λ1 = 577 nm), however, a discrepancy between the experimental curve and the theoretical prediction (upper panel, Fig. 13) becomes noticeable, presumably due to the involvement of v′ ≥ 40 states.

In the frequency domain (cf. Fig. 14), the experimental
and calculated wave packet transients for $\lambda_1 = 600$ nm are also in excellent agreement. The experimental profile is broader than the simulated version but otherwise the theory matches the data remarkably well. Both the peak at $17.0 \text{ cm}^{-1}$ and the weak pedestal lying at $14 \text{ cm}^{-1}$ are reproduced by the calculations. When $\lambda_1 = 577$ nm, on the other hand, the theoretical spectrum is shifted $0.7 \text{ cm}^{-1}$ to lower energy with respect to the experimental curve. This discrepancy appears to be directly attributable to the perturbation of the $D^1\Sigma_u^+$ state discussed earlier. The near reproduction of the experimental data by the simulations is actually remarkable when one considers that the $D$ state wave packet is composed of a minimum of 20 vibrational states, and is a reflection of the precision of the experiments in Refs. 20–23 and 27.

### IV. CONCLUSIONS

The temporal behavior of vibrational wave packets produced in the $B^1\Pi_u$ and $D^1\Sigma_u^+$ states of Cs$_2$ has been studied by pump–probe laser spectroscopy on the $\sim 100$ fs time scale. The $C^1\Pi_u$ state was chosen in Refs. 3 and 4 for initial experiments in this molecule for several reasons: (1) the large difference ($\sim 0.75 \text{ Å}$) between $R_e$ for the $C$ state relative to that for Cs$_2^+(X)$, which results in photoionization of $C^1\Pi_u$ in a narrow corridor near the classical inner turning points for the Cs$_2^+$ ($v^+ = 65–90$) vibrational levels and a large modulation depth of the photoionization signal; (2) despite being weakly predissociated, $C^1\Pi_u$ is relatively unperturbed and has been thoroughly characterized by high resolution laser spectroscopy; and (3) the $C \rightarrow X$ transition is conveniently situated for excitation by a CPM system. In contrast, the equilibrium internuclear separations for the $B^1\Pi_u$ and $D^1\Sigma_u^+$ states differ from that for the Cs$_2^+$ ground state by $0.38 \text{ Å}$ and $0.43 \text{ Å}$, respectively, or roughly half that for the $C$ state. Also, $R_{eB} - R_e(Cs_2^+) < 0$ whereas $R_{eD} - R_e(Cs_2^+) > 0$. Consequently, the Cs$_2$ $B$ and $D$ states afford an opportunity to evaluate the wave packet detection approach introduced in Ref. 3—namely, monitoring the time and energy-integrated photoelectron current. As expected,
The frequency composition of the D state vibrational wave packets is in accord with potentials and spectroscopic constants determined by laser spectroscopy in the frequency domain. It also appears that vibrational wave packets in the D state provide a tool for observing the $D^1\Sigma_u^+ \rightarrow 2^3\Pi_{0u}$ interaction.

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