Structure of excitation and fluorescence spectra recorded at the ${}^{1}0_{u}^{+}(5 {}^{1}P_{1}) - X {}^{1}0_{g}^{+}$ transition of Cd₂

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Excitation and fluorescence ultraviolet spectra of Cd₂ recorded at the ${}^{1}0_{\mu}^{+}(5 {}^{1}P_{1}) - X {}^{1}0_{\rho}^{+}$ transition are reported. The Cd₂ molecules (seeded in Ar) produced in a continuous free-jet supersonic beam were excited in a vacuum chamber with a pulsed dye-laser beam. A well-resolved vibrational structure of the ${}^{1}O_{u}^{+} \leftarrow X {}^{1}O_{e}^{+}$ excitation spectrum as well as the isotopic structure of the vibrational components were recorded. Analysis of the spectrum yielded vibrational constants for the ${}^{1}O_{u}^{+}$ state: $\omega'_{e} = 100.50 \pm 0.25 \text{ cm}^{-1}$, $\omega'_{e}x'_{e} = 0.325 \pm 0.003 \text{ cm}^{-1}$, $D'_{0} = 8638 \pm 15 \text{ cm}^{-1}$, $D'_{e} = 8688 \pm 15 \text{ cm}^{-1}$, and $\Delta R_{e} = R''_{e} - R'_{e} = 1.04 \pm 0.01 \text{ Å}$ derived for the 226 Cd₂ isotopomer. The $^{10}u^{+}$ state potential-energy (PE) curve was obtained numerically using an inverse perturbation approach (IPA) procedure. Condon internal diffraction (CID) patterns in the ${}^{1}0_{\mu}^{+} \rightarrow X {}^{1}0_{\mu}^{+}$ fluorescence band, emitted upon the selective excitation of the v' = 38 and v' = 39 vibrational components of the 226 Cd₂ isotopomer, were observed and improved the v' assignments derived from the analysis of the isotopic structure. Analysis of the fluorescence spectrum yielded information on the repulsive part of the ground-state interatomic potential. The result confirms a relatively soft repulsion between two Cd atoms in the short-range (2.53-4.05 Å) region and makes allowance for a covalent admixture to the ground-state van der Waals bonding. Quasirelativistic valence ab initio calculations on the PE curves for the investigated states have been performed at the complete-active-space multiconfiguration self-consistent-field (CASSCF/CAS) multireference second-order perturbation theory (CASPT2) level with the total of 40 correlated electrons. In the calculations, the Cd atom is considered as a 20-valence electron system whereas the Cd²⁰⁺ core is replaced by an energyconsistent pseudopotential which also accounts for scalar-relativistic effects and spin-orbit interaction within the valence shell. A comparison with results obtained from other experiments and *ab initio* calculations is presented.

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I. INTRODUCTION

Early investigations of absorption and fluorescence of cadmium vapors were performed at the beginning of the twentieth century [1]. Soon after, the molecular absorption and the fluorescence spectra of Cd2 were recorded by Kapuściński [2], Mohler and Moore [3], Jabłoński [4], Mrozowski [5], Hamada [6], and Cram [7]. The studies concluded with information on the location of the detected spectra and their origin. Approximate depths and equilibrium internuclear distances for the ground- and several excited-state potential energy (PE) curves were also given [7]. Ultraviolet absorption spectra of Cd₂ in solid Ar and Kr were reported in a series of experiments by Andrews and co-workers [8,9]. The absorption profile of the 5 ${}^{1}P_{1}$ – 5 ${}^{1}S_{0}$ Cd resonance line broadened by pressure effects of Cd was measured by Bousquet [10], providing molecular constants for the $X^{1}0_{p}^{+}$, as well as ${}^{1}0_{u}^{+}(5 {}^{1}P_{1})$ and ${}^{1}1_{u}(5 {}^{1}P_{1})$ excited electronic energy states [Hund's case (c) notation, spin-orbit coupling included].

The laser excitation spectrum of the ${}^{3}0_{u}^{+}(5 {}^{3}P_{1}) \leftarrow X {}^{1}0_{g}^{+}$ transition in Cd₂ produced in a supersonic beam was reported by Kowalski *et al.* [11]. The same transition

was further investigated by Czajkowski et al. [12] using a similar experimental approach. Both reports assumed Morse representations for the ground- and excited-state interatomic potentials below their dissociation limits. However, in the more advanced approach [12] the ground-state characterization was indirect and the equilibrium internuclear separations $R'_{e}({}^{3}0'_{u})$ and R''_{e} were estimated from the difference ΔR_{e} $=R'_{e}-R''_{e}$, obtained in a simulation of the Franck-Condon factors (F-CF) intensity distribution. References [11] and [12] are the only experimental studies of Cd₂ produced in supersonic beams that had been carried out before the work of Czajkowski and Koperski [13] and Koperski et al. [14]. The former presents a corrected characterization of the ground-state potential well based on "hot" bands detected in excitation at the ${}^{3}O_{u}^{+} \leftarrow X {}^{1}O_{g}^{+}$ transition (the ground-state Morse representation was determined up to 40 cm⁻¹ from the bottom of the potential well), while the latter reports on a characterization of the ${}^{3}1_{u}(5 {}^{3}P_{2})$ state. Among other reliable results related to the laser spectroscopy of Cd₂ are those of Eden and co-workers [15,16]. Two, $B^{-1}\Sigma_{u}^{+}(5^{-1}P_{1})$ and $a {}^{3}\Pi_{g}(5 {}^{3}P_{1})$ excited states, and the repulsive part of the $X^{1}\Sigma_{g}^{+}$ ground state in Cd₂ [Hund's case (a) notation, without spin-orbit coupling] were investigated in Cd vapors [16]. A more detailed study of Cd2 bound-free emission in $B^{-1}\Sigma_{u}^{+} \rightarrow X^{-1}\Sigma_{g}^{+}$ transition were also reported [15]. The main conclusion drawn from the investigation was that the

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ground-state repulsive part is represented by a Morse function. The electron beam excitation of Cd₂ was studied by Xing et al. [17], particularly the bound-free emission in the ${}^{3}\Sigma_{u}^{+}(n {}^{3}P) \rightarrow X {}^{1}\Sigma_{g}^{+}$ transition. Those studies were driven by a search for an effective energy reservoir in a possible tunable laser medium (excimer). Results of an ab initio calculation of the Cd₂ PE curves available in the literature are those of Bender et al. [18] and Czuchaj et al. [19], Schautz et al. [20], Yu and Dolg [21], and Garcia de la Vega and Miguel [22]. Bender et al. performed full configurationinteraction (CI) calculations for the four valence electrons of the Cd₂ species working in a Gaussian basis set. Czuchaj et al. derived the Cd₂ PE curves and dipole transition moment $M_{z}(R)$ for a number of electronic states using the multireference configuration-interaction (MRCI) [single and double excitation (SD)] procedure for the valence electrons, while the core electrons were represented by semiempirical l-dependent pseudopotentials. The effect of spin-orbit coupling was not investigated. Pure diffusion quantum Monte Carlo (PDCM) techniques were applied by Schautz et al. together with relativistic large-core pseudopotentials and corepolarization potentials to yield accurate molecular constants for 12-group homonuclear metal (M) dimmers (Zn_2 , Cd_2) and Hg₂). They also investigated the transition from van der Waals (vdW) to covalent and finally metallic bonding. The covalent contribution to the vdW bonding was calculated by Yu and Dolg using atom-base local occupation number operators and associated interatomic charge fluctuations at the complete-active-space multiconfiguration self-consistent field (CASSCF).

In a very weakly bound ground state of the 12-group M_2 dimers, the long-range interaction is dominated by dispersion forces as expected from the simple consideration of the closed-shell atomic configurations [23]. Recent ab initio calculations of the components of the interaction energy in the ground state of mercury dimer [24] show that short-range induction effects play a significant role in the stabilization of Hg_2 . Therefore, the Hg_2 may be regarded as an intermediate case between a weakly bound vdW molecule and a chemically bound species (e.g., [25]). The same behavior has been inferred from *ab initio* calculations of Zn₂ and Cd₂ [21,26]. The studies [20,21,26] resulted in a clear conclusion that the 12-group homonuclear dimers, although a vdW-type interaction, exhibit the presence of significant covalent contributions to the binding. Moreover, it was found experimentally [27] that the repulsive part of the Hg₂ ground state is unusually soft (as compared, for example, with the MRG or RG_2) ground-state repulsive walls, where RG is a rare gas atom [23]). A covalent binding contributes to the net forces acting between two Hg atoms also in the intermediate region of internuclear separations (near the $R_{e}^{"}$) [20,28]. To account for this behavior, in an interpretation of a collision-induced depolarized Raman scattering from dense mercury vapor in Ref. [28], a special damping term was included into the Hg₂ interatomic potential for suppression of the dispersion part at close range. It is expected that similar experimental confirmation of the theoretical predictions will be found for the remaining 12-group dimers.



FIG. 1. Simplified interatomic potential scheme for Cd₂. Three electronic energy states, ${}^{3}O_{u}^{+}(5 {}^{3}P_{1})$, ${}^{3}1_{u}(5 {}^{3}P_{2})$, and ${}^{1}O_{u}^{+}(5 {}^{1}P_{1})$, directly accessible from the $X {}^{1}O_{g}^{+}(5 {}^{1}S_{0})$ ground state, are depicted along with wavelengths at which the corresponding excitation spectra are centered. A range of vibrational levels v' in the ${}^{1}O_{u}^{+}$ state (dashed horizontal lines) reachable in the excitation from the v''=0, as well as florescence (wide block arrow) emitted upon a selective excitation of the particular v' are shown. For the sake of simplicity, all PE curves are represented by Morse functions. *Ab initio* calculated points of this work (full circles) for the excited states are also shown.

of a degree of the Cd-Cd repulsion in the short-range limit from a modeling of the fluorescence profiles recorded at the ${}^{1}0_{u}^{+}(5 {}^{1}P_{1}) \rightarrow X {}^{1}0_{g}^{+}$ transition in Cd₂ (natural abundance) produced in supersonic expansion beams. Furthermore, the detected excitation spectrum at the ${}^{1}0_{u}^{+} \leftarrow X {}^{1}0_{g}^{+}$ transition with a resolved isotopic structure was analyzed, making possible characterization and analytical representation of the excited-state PE curve. A simplified interatomic potential scheme for Cd_2 is shown in Fig. 1. Three electronic energy states (ungerade) directly accessible from the ground state (gerade) were depicted only. Two of them, ${}^{3}O_{\mu}^{+}(5 {}^{3}P_{1})$ [11,12] and ${}^{3}1_{\mu}(5 {}^{3}P_{2})$ [14], were already characterized spectroscopically in experiments of crossed molecular and laser beams. The remaining one, ${}^{1}0_{\mu}^{+}(5 {}^{1}P_{1})$, is a subject of this study. Our experimental studies stimulated in turn some improvements of the ab initio calculations of earlier theoretical work [19] leading to a better experiment-to-theory agreement and, hence, to a better understanding of the nature of Cd₂ bond.

This paper is organized as follows. *Ab initio* calculations of the ground-state and few low-lying excited-state interatomic potentials as well as of the dipole moment for the ${}^{1}O_{u}^{+}-X {}^{1}O_{g}^{+}$ transition are presented in Sec. II. Section III is devoted to the description of experimental details while in Secs. IV and V the excitation and fluorescence spectra are discussed, respectively. Section VI concludes the paper.

II. AB INITIO CALCULATIONS

A. Method

In the Born-Oppenheimer approximation the adiabatic energies of a molecular system are obtained as a result of solving the Schrödinger equation with the total Hamiltonian

$$H = T + V, \tag{1}$$

where *T* stands for the kinetic energy operator of the valence electrons and *V* represents the interaction operator. In the present approach the 4s4p4d5s electrons of the Cd atom are treated explicitly. That means that the Cd₂ dimer is considered as a 40-valence electron species. On the other hand, the Cd²⁰⁺ core as well as valence-shell scalar-relativistic effects and spin-orbit (SO) interaction are represented by *ab initio lj*-dependent quasirelativistic energy-consistent pseudopotentials. The interaction operator in Eq. (1) in atomic units is set as

$$V = V_{av} + V_{SO} + \sum_{j>i=1}^{N} \frac{1}{r_{ij}} + \frac{Q_1 Q_2}{r_{12}},$$
 (2)

where *i*, *j* denote valence electrons and Q_1 , Q_2 represent core charges. The SO-averaged pseudopotential V_{av} , which accounts for scalar-relativistic effects, has the following semilocal form:

$$V_{av} = -\sum_{\lambda,i} \frac{Q_{\lambda}}{r_{\lambda i}} + \sum_{\lambda,i} \sum_{l,k} A_{\lambda lk} \exp(-a_{\lambda lk} r_{\lambda i}^2) P_{\lambda l}, \quad (3)$$

where $P_{\lambda l}$ is the projection operator onto the Hilbert subspace of angular symmetry *l* with respect to core λ ($\lambda = 1,2$)

$$P_{\lambda l} = \sum_{m=-l}^{l} |\lambda lm\rangle \langle \lambda lm|.$$
(4)

In turn, the pseudopotential representing the SO operator takes the form

$$V_{SO} = \sum_{\lambda,i} \sum_{l} \frac{2\Delta V_{i,\lambda l}}{2l+1} P_{\lambda l} \mathbf{l}_{i} \mathbf{s}_{i} P_{\lambda l} \,. \tag{5}$$

The difference $\Delta V_{i,\lambda l}$ of the radial parts of the twocomponent quasirelativistic pseudopotentials $V_{\lambda l,l+1/2}$ and $V_{\lambda l,l-1/2}$ is written similarly to the radial part of the spinorbit averaged pseudopotential V_{av} in terms of Gaussian functions

$$\Delta V_{i,\lambda l} = \sum_{k} \Delta A_{\lambda lk} \exp(-a_{\lambda lk} r_{\lambda i}^{2}).$$
 (6)

In the case of small-core pseudopotentials (as in the present case) the polarization potential that describes, among others, core-valence correlation effects is usually disregarded, because the dipole polarizabilities of the cores are too small. The last term in Eq. (2) represents the core-core interaction. Since the two Cd^{20+} cores are assumed to be well separated, we choose a simple point-charge Coulomb interaction in this case.

B. Details of calculations

High-level valence ab initio calculations have been carried out for the ground state and the excited states of the Cd₂ species correlating with the $(5p)^3P + {}^1S$ and $(5p)^1P + {}^1S$, asymptotes. The present calculations on Cd₂ are superior to the earlier studies [19] where the Cd atom was treated as a two-valence electron system and SO coupling was neglected. The free parameters in the radial parts of the pseudopotentials, as defined by Eqs. (3), (5), and (6), are taken from [29]. The SCF-energy-optimized uncontracted (8s7p6d) Gaussian basis set for Cd from [29] was augmented by one diffuse function for s, p, and d symmetries (exponents 0.006282, 0.012 638, 0.025 128, respectively). In addition, a set of four polarization f functions (exponents 4.5, 1.5, 0.5, 0.17) and two sets of g functions (exponents 1.5, 0.5) were added to the basis as described in Ref. [30]. Finally, in the calculations we used the contracted (9s8p7d4f2g)/[8s7p6d4f2g] basis set. The quality of the present 20-valence electron model, including SO coupling, was verified in atomic CI calculations for the ground and several excited states of the Cd atom [30].

The PE curves have been first evaluated at the completeactive-space multiconfiguration self-consistent-field (CASSCF)/CAS multireference second-order perturbation theory (CASPT2) level with an open-shell correction term to the one-electron Fock operator as proposed by Werner [31]. The active space was spanned by the molecular counterparts of the Cd 5s5p and 6s6p orbitals in the D_{2h} point group. It turns out that including the 6p orbitals substantially improves agreement of the calculated Cd (5s5p) ³P and ¹P atomic energies with experimental values. The molecular orbitals were determined in a state-averaged CASSCF with the same weight for the ground and excited states. The next step in the calculations involves the inclusion of SO coupling. The SO eigenstates were obtained by diagonalizing the H_{el} $+H_{so}$ matrix in a basis formed of selected spatial configurations multiplied with appropriate spin eigenfunctions. The resulting products are grouped together according to symmetry to form an appropriate matrix for each representation of the D_{2h} double group. In the present calculations the offdiagonal elements of the SO operator are computed employing the truncated version of the CI space restricted to the CASSCF wave functions. However, to account for correlation effects at a higher level of theory, the diagonal elements of the SO matrix before diagonalization were replaced by the precomputed CASPT2 eigenenergies. Finally, the calculated potential curves have been corrected for the basis set superposition error (BSSE) using the standard counterpoise method of Boys and Bernardi [32]. The calculations have been performed by means of the MOLPRO program code by Werner and Knowles [33–36].

C. Results and discussion of calculations

The molecular calculations have been performed for the Cd-Cd internuclear separations ranging from 4.0 to $40a_0$

(where $a_0 = 0.529 \ 177$ Å is a Bohr radius) with different step sizes. The calculations involve molecular states correlating with the Cd atomic states from the $(5s^2)$ ¹S ground to the (5s5p) ¹P excited state. The PE were calculated with respect to the energy of the separated atoms at $R = 100a_0$. Numerical values of the potential curves are available from the authors (E.C.) upon request. The potential-well depths D_e and equilibrium internuclear separations R_e were derived using a cubic spline approximation to the calculated potential energies around their equilibrium separations. In turn, the fundamental frequencies ω_e were calculated by numerical solving the radial Schrödinger equation for nuclear motion with the corresponding potential. For this purpose the Numerov-Cooley method was applied.

1. Ground state

The $X^{1}\Sigma_{g}^{+}$ ($\Omega=0$) ground state of Cd₂ arises from two $(5s^2)^1S$ Cd atoms and is represented primarily by the single configuration wave function (core) $10\sigma_a^2 10\sigma_u^2$, where (core) represents the electronic configuration of the inner shell electrons. For the ground state, the only possible long-range attractive force between the two atoms is due to the dispersion interaction caused by correlation between the fluctuating multipolar charge distributions of the atoms. Covalent bonding contributes *significantly* to the interaction energy in the region of intermediate internuclear separations where the molecule is formed. The CASSCF/CASPT2 ground-state potential curve for diatomics is thought not to be as accurate as that resulting from other more sophisticated calculations. Therefore, to yield a more reliable ground-state potential curve for Cd₂ we have applied the single-reference coupledcluster approach with single and double excitations, including a perturbative estimate of triple excitations [CCSD(T)]method for 40 correlated electrons. The CCSD(T) scheme is currently considered as one of the most accurate singlereference methods and is feasible with the MOLPRO code. The calculated CCSD(T) ground-state potential curve for Cd₂ (points) is compared with the experimental result below (see Sec. V and Table IV). The minimum of the potential curve corrected for BSSE is characterized by $D''_e = 287.3 \text{ cm}^{-1}$, $R''_e = 7.53 \ a_0$ (3.98 Å), and $\omega''_e = 19.2 \text{ cm}^{-1}$. It has to be noted that the obtained R''_e is *shorter* than that of Ref. [13] $(R''_e = 4.07 \text{ Å})$ estimated assuming a pure long-range vdW interaction between two ground-state Cd atoms [37,38]. According to the conclusions from ab initio calculations of this work and those of Ref. [20], this may confirm a covalent contribution to the ground-state bonding.

2. Excited states

The long-range part of the interaction of two like atoms being in different energy states is dominated by the electrostatic dipole-dipole resonance energy. The leading term of the first-order dipole-dipole resonance energy is proportional to the $M_z^2 R^{-3}$ term, where M_z^2 is the square of the dipole transition moment between the ground and the excited state of the atom. Investigated in this work the ${}^{1}\Sigma_{u}^{+}$ [in Hund's case (a)] excited state strongly couples with the ground state as a result of electric dipole transition. Asymptotically, the

 ${}^{1}\Sigma_{u}^{+}$ state is ascribed to the ${}^{1}P + {}^{1}S$ atomic limit and is represented by the $10\sigma_g^2 10\sigma_u 13\sigma_g$ and $10\sigma_g 10\sigma_u^2 13\sigma_u$ configurations. The long-range part of its interaction energy is dominated by the $-2M_z^2 R^{-3}$ term. Due to a large energy gap (31246 cm^{-1}) between the triplet state and the ground state of the Cd atom, the influence of SO interaction on the ground state is negligible. However, SO coupling mixes the ${}^{3}\Pi_{u}$ and ${}^{3}\Sigma_{u}$ states to yield the appropriate Ω states. Also, the contribution to the triplet state arising from SO interaction with the upper singlet (5s5p) ¹P state proves to be of minor importance. In consequence, both the ground state and the two ${}^{1}\Sigma_{u}^{+}$ singlet states of Cd₂ remain almost unchanged due to SO interaction, whereas the appropriate Ω -potential curves correlating with the fine-structure components of the Cd atom differ considerably from the ${}^{3}\Pi_{u}$ and ${}^{3}\Sigma_{u}$ curves. The points of Ω -potential curves [in Hund's case (c)] resulting from diagonalization of the $H_{el} + H_{SO}$ matrix for the previously experimentally investigated states [11,12,14] are shown in Fig. 1. The molecular states that correlate with the Cd ${}^{3}P_{1} + {}^{1}S$ and ${}^{3}P_{2} + {}^{1}S$ asymptotes are labeled ${}^{3}O_{u}^{+}$ and ${}^{3}1_{\mu}$, respectively. Simultaneously with the potential curves, the dipole transition moment M_z between the ground state and the excited singlet $(5p)^1 \Sigma_u^+$ state (without and with, i.e., $\Omega = 0$, spin-orbit coupling) has been evaluated at the CASSCF level. The result is shown in one of the insets of Fig. 7. As seen, the calculated transition moment exhibits a rather strong dependence on R in the range of short internuclear separations. Surely, these results can prove to be of importance for study of the spectra arising from the Cd₂ dimer.

III. EXPERIMENTAL DETAILS

The experimental procedure was described elsewhere [39-41]. The experiments were carried out independently in two laboratories, in Kraków and Windsor, and details of both experimental setups are discussed thoroughly in Ref. [23]. Here, we describe only the most important and most relevant modifications which were employed in the studies reported below. Laser-induced fluorescence (LIF) was observed in an evacuated expansion chamber into which the Cd atoms (natural abundance) seeded in Ar were injected through a nozzle (150 μ m in diam, D) constituting part of the molecular beam source. The Cd₂ molecules in the beam were irradiated with a third harmonic output of a Nd⁺: YAG (yttrium aluminum garnet) laser-pumped dye laser (dyes: Coumarine 500 and 540 A). A BBO-C frequency doubling crystal used in conjunction with the dye laser was scanned by a computer program simultaneously with the dye-laser dispersion element over the range 2500-2700 Å. The frequency calibration of the dye laser was verified with 1.5 cm^{-1} and 0.03cm⁻¹ accuracy against a WA 4500 pulsed wave meter (Burleigh), and optogalvanic cells with Ne and Ar (Sirah), respectively. The spectral linewidth of the dye-laser fundamental output was estimated with the help of a monitor etalon (free spectral range of 0.33 cm⁻¹) and was found to be approximately 0.25 cm^{-1} .

The resulting excitation spectra were monitored with a



FIG. 2. The ${}^{1}0_{u}^{+}, v' \leftarrow X {}^{1}0_{g}^{+}, v''=0$ transition in an excitation spectrum of Cd₂ (the left part shows detail for the v'=38-40). (a) Experimental trace showing v' assignments; effective distance from the nozzle $X_{eff}=6$ mm, pressure of the carrier gas $p_{Ar}=12$ atm, temperature of the source oven $T_0=870$ K, n_0 density number of Cd atoms in the source oven $n_0\approx 6\times 10^{17}$ cm⁻³, and the density number in the region of excitation $n(X_{eff}=6 \text{ mm})\approx 10^{13} \text{ cm}^{-3}$; laser dye: Coumarine 500 (the long-wavelength part of the spectrum was recorded in a separate experiment with Coumarine 540 A). (b) Computer-simulated [49] spectrum showing the "best fit" to the $v' \leftarrow v''=0$ progression obtained for $\Delta R_e = 1.04 \pm 0.01$ Å; the simulation includes the isotopic composition of each vibrational component assuming turning-point pairs from the IPA procedure and Morse representations for the excited and ground states, respectively; the relative positions of the isotopic peaks were calculated using Eq. (7), and their amplitudes were weighted relative to the total relative abundances of particular isotopes in natural cadmium (see Table I; for more details of the simulation see the text). Here, the individual (A_1+A_2) isotopic peaks were represented by a Lorentzian curve with full width at half maximum (FWHM) of 2.3 cm⁻¹. The rotational structure of the isotopic components was not simulated. (c) Amplitudes of (A_1+A_2) isotopic components drawn in order to show their overlap for neighboring v'.

photomultiplier (PM) tube (Schlumberger EMR-541-N-03-14 in Windsor or Electron Tubes 9893QB/350 in Kraków) at right angles to the plane containing the crossed molecular and laser beams. The fluorescence spectra were recorded with the laser wavelength set on a particular isotopic component of vibronic transition. Fluorescence from the interaction region in the beam was focused on the entrance slit of an HR-640 Czerny-Turner (Jobin-Yvon) with 2400 grooves/mm grating (in Windsor) or an Ebert-500 (Jarrel Ash) with 1800 grooves/mm grating (in Kraków) monochromator (MON) that was fitted with the respective PM. The PM signal was recorded with a transient digitizer and stored in a computer. The PM-MON system was wavelengthcalibrated using Hg and Hg+Cd spectral lamps. With the help of a deuterium calibration lamp, the systems were intensity-calibrated and spectral response characteristics for both systems were found to be virtually flat in the wavelength region of interest.

IV. THE EXCITATION SPECTRUM

A search for the ${}^{1}0_{u}^{+} \leftarrow X {}^{1}0_{g}^{+}$ transition in excitation began with a simulation of the F-CF intensity distribution using *ab initio* calculated points (see Fig. 1) and Morse representation [13] of interatomic potentials for the excited and ground states, respectively. It was found that the intensity distribution should expand in the region 2530–2630 Å with a maximum around 2580 Å. Figure 2(a) presents the recorded excitation spectrum. The spectrum consists of 36 structured vibrational components (from v' = 19 to v' = 54) belonging to the $v' \leftarrow v'' = 0$ progression. Figure 2(b) shows a simulation of the spectrum, which will be described in details below. As shown in the inset of Fig. 2 and in Fig. 3, each of the vibrational components consists of eighteen peaks corre-

sponding to the different $(A_1 + A_2)$ combinations $(A_1 \text{ and } A_2)$ are the Cd mass numbers in the Cd₂ molecule) of the eight stable Cd isotopes {^ACd (p = abundance in %): ¹⁰⁶Cd (p=1.22), ¹⁰⁸Cd (0.88), ¹¹⁰Cd (12.39), ¹¹¹Cd (12.75), ¹¹²Cd (24.07), ¹¹³Cd (12.26), ¹¹⁴Cd (28.86), and ¹¹⁶Cd (7.58)} present in natural cadmium [42] (for details see Table I). A Birge-Sponer (BS) plot drawn for isotopic peaks that belonged to the ${}^{226}Cd_2$ isotopomer (${}^{226}Cd_2$ originates from the ¹¹⁰Cd¹¹⁶Cd, ¹¹²Cd¹¹⁴Cd, and ¹¹³Cd¹¹³Cd combinations) is shown in Fig. 4 (see also Table II). In the range of recorded vibrational components, the BS plot is linear and, therefore, was used for the determination of the fundamental vibrational frequency ω'_0 and anharmonicity $\omega'_0 x'_0$ (a slope) of the isotopomer [43]. As a result, in anharmonic oscillator approximation, the $\omega'_e = 100.50 \pm 0.25 \text{ cm}^{-1} (\omega'_e \approx \omega'_0 + \omega'_0 x'_0)$ and $\omega'_e x'_e = 0.325 \pm 0.003 \text{ cm}^{-1}$ ($\omega'_e x'_e \approx \omega'_0 x'_0$) were obtained. The approximation $[D'_i \approx (\omega')_i^2/4\omega'_i x'_i]$, where i=0or i = e [43]] yields also the dissociation energy and well depth, $D'_0 = 7723 \pm 15 \text{ cm}^{-1}$ and $D'_e = 7773 \pm 15 \text{ cm}^{-1}$, respectively, the values which will be compared with other estimates below.

The $v' \leftarrow v''=0$ and $v' \leftarrow v''=1$ progressions from the metastable $a {}^{3}\Pi_{g}$ state to lower-lying (v'=0-31) vibrational levels of the ${}^{1}\Sigma_{u}^{+}(\Omega=0)$ state were reported by Tran and Eden [16] as a result of the pump-and-probe experiment in Cd vapors (natural abundance). Consequently, they obtained somewhat different values for ω_{e}' and $\omega_{e}'x_{e}'$, which are compared in Table III with the results of the present study.

The v' assignments of the vibrational components in the excitation spectrum were carried out by analyzing their isotopic shift Δv_{ij} which, for $v' \leftarrow v''=0$ vibronic transitions, may be represented by [43]



FIG. 3. The isotopic structure of the v' = 40 vibrational component of the spectrum from Fig. 2. (a) Experimental trace; (A_1) $+A_2$) for isotopic components are depicted. (b) Amplitudes of all elementary components with different (m_1+m_2) mass combinations within each of the (A_1+A_2) isotopic peak showing complexity of one vibrational component (see also Table I). (c) Simulation of the rotational structure of each of the $(m_1 + m_2)$ elementary components (P and R branches; the Q branch is not present); $B_{n'=40}$ = 0.0208 cm⁻¹ and $B_{v''=0}$ = 0.0136 cm⁻¹ rotational constants were calculated using the formula [43] $B_v \approx h/8 \pi^2 c \mu R_e$ [1] $-\omega_e x_e/\omega_e(v+1/2)$], where h and c are the Planck constant and the speed of light, respectively; R_e , ω_e , and $\omega_e x_e$ are taken from Tables III and IV; dependencies $B_e^{isot} = \rho^2 B_e$ and $\alpha_e^{isot} = \rho^3 \alpha_e$, where the superscript "isot" denotes the constant for different isotopomers. The missing of every alternate line in the branches for each A-like isotopomer and intensity alteration that depends on the statistics of the nuclei [43] were not taken into account as negligible in this approximation. To clarify the picture each rotational component is represented by a short vertical line. (d) Final simulation obtained by representing each of the rotational components in (c) with a Lorentzian curve with FWHM of 0.3 cm^{-1} .

$$\Delta \nu_{ij}(v',v''=0) = \omega'_e(1-\rho)\left(v'+\frac{1}{2}\right) - \omega'_e x'_e(1-\rho^2)\left(v'+\frac{1}{2}\right)^2 - \frac{\omega''_e(1-\rho)}{2} + \frac{\omega''_e x''_e(1-\rho^2)}{4},$$
(7)

where $\rho = \sqrt{\overline{\mu}_i/\overline{\mu}_j}$, $\overline{\mu}_i$ and $\overline{\mu}_j$ are the averaged reduced masses of *i* and *j* isotopomers of Cd₂ with different (A₁ +A₂) combinations, and ω'_e and $\omega'_e x'_e$ were taken from the above BS analysis, whereas ω''_e and $\omega''_e x''_e$ are vibrational frequency and anharmonicity of the $X^{10}_{g}^{+}$ state [13]. As

TABLE I. Eight stable isotopes of Cd with mass numbers (A) and atomic masses (m_A in amu): $m_{106}=105.906$, $m_{108}=107.904$, $m_{110}=109.903$, $m_{111}=110.904$, $m_{112}=111.902$, $m_{113}=112.904$, $m_{114}=113.903$, $m_{116}=115.905$, as well as their combinations with reduced masses (μ in amu), and 18 different mass-number ($A_1 + A_2$) and averaged-reduced-mass ($\bar{\mu}$ in amu) combinations with relative total abundances (in %).

<i>A</i> ₁	A_2	μ	$A_1 + A_2$	μ	Relative total abundance	
106	106	52.953	212	52.953	0.024	
106	108	53.448	214	53.448	0.018	
106	110	53.934	216	52 042	0.260	
108	108	53.952	210	33.945	0.200	
106	111	54.174	217	54.174	0.255	
106	112	54.411	218	54 420	0.650	
108	110	54.447	210	54.429	0.039	
106	113	54.647	210	54 670	0.664	
108	111	54.692	219	54.070	0.004	
106	114	54.880				
108	112	54.933	220	54.922	3.150	
110	110	54.952				
108	113	55.174	221	55 199	2 760	
110	111	55.201	221	55.100	2.700	
106	116	55.340				
108	114	55.411	222	55 413	8.104	
110	112	55.447		55.415		
111	111	55.452				
110	113	55.692	223	55.696	9.898	
111	112	55.700	225	55.070	2.020	
108	116	55.881				
110	114	55.934	224	55 929	17 991	
111	113	55.948	224	55.727	17.991	
112	112	55.951				
111	114	56.192	225	56 196	10.846	
112	113	56.200	225	50.170		
110	116	56.412				
112	114	56.447	226	56.437	15.357	
113	113	56.452				
111	116	56.675	227	56 688	7 368	
113	114	56.701		20.000	7.500	
112	116	56.934	228	56 943	16 608	
114	114	56.952	220	50.715	10.000	
113	116	57.192	229	57.192	1.520	
114	116	57.448	230	57.448	3.578	
116	116	57.953	232	57.953	0.940	

shown in Fig. 5, the averaged measured isotopic shifts were found to be in the range $3.9-8.1 \text{ cm}^{-1}$. The averages were taken between peaks corresponding to $(A_1+A_2)=222$ and 223, 223 and 224, 224 and 225, 225 and 226, 226 and 227, and 227 and 228. We have also plotted the shifts calculated from Eq. (7) for v' (our assignment) as well as for v'+3and v'-3. We found that the plot of the measured isotopic shifts against the v' given by the analysis lies within the limits of the shifts calculated for $v'\pm 3$, indicating that at this



FIG. 4. A Birge-Sponer plot drawn for isotopic peaks belonged to the ²²⁶Cd₂ isotopomer in the $v' \leftarrow v'' = 0$ progression of the ${}^{1}0^{+}_{u} \leftarrow X {}^{1}0^{+}_{g}$ excitation spectrum. The dashed line represents a "short" extrapolation which enabled us to determine the ω'_{0} (an intercept with a vertical axis). The upper and lower insets show $\omega'_{e}x'_{e}(\rho^{2})$ and $\omega'_{e}(\rho)$ dependencies, respectively, drawn for all different $[(A_{1}+A_{2}) \text{ from 212 to}$ 232] isotopic combinations.

stage of the analysis our v' assignments are correct within the mentioned error margin. It has to be noted here that because the BS plot analysis involved only the ²²⁶Cd₂ isotopomer, the ω'_e and $\omega'_e x'_e$ vibrational constants for the remain-

ing isotopomers differ from these for the ²²⁶Cd₂ one according to $(\omega'_e)^{\text{isot}} = \rho \omega'_e$ and $(\omega'_e x'_e)^{\text{isot}} = \rho^2 \omega'_e x'_e$ [43], where the superscript "isot" denotes the constant for the remaining isotopomer. Considering differences between the

TABLE II. Experimental $(\nu_{expt}\pm 0.2 \text{ cm}^{-1})$ and calculated (ν_{calc}) results using the inverse perturbation approach procedure frequencies for the ${}^{226}\text{Cd}_2$ isotopomer of the $v' \leftarrow v'' = 0$ vibronic progression of the ${}^{1}0^+_u \leftarrow X {}^{1}0^+_g$ transition in Cd₂. $\nu_{expt} - \nu_{calc}$ is also shown.

υ'	$ u_{\mathrm{expt}}$	$ u_{\mathrm{calc}}$	$\nu_{\rm expt} - \nu_{\rm calc}$	υ'	$ u_{\mathrm{expt}}$	$ u_{\rm calc} $	$v_{\rm expt} - v_{\rm calc}$
0		35368.8					
1		35468.6		28	37926.4	37925.5	+0.9
2		35567.8		29	38008.5	38007.3	+1.2
3		35666.4		30	38090.5	38088.7	+1.8
4		35764.3		31	38169.7	38168.8	+0.9
5		35861.5		32	38248.9	38248.5	+0.4
6		35958.1		33	38329.1	38327.5	+1.6
7		36054.1		34	38406.8	38405.8	+1.0
8		36149.4		35	38484.2	38483.4	+0.8
9		36244.0		36	38561.4	38560.4	+1.0
10		36338.0		37	38638.4	38636.7	+1.7
11		36431.4		38	38712.4	38712.3	+0.1
12		36524.1		39	38785.5	38787.2	-1.7
13		36616.1		40	38861.0	38861.5	-0.5
14		36707.5		41	38935.5	38935.1	+0.4
15		36798.7		42	39007.6	39008.1	-0.5
16		36889.6		43	39079.3	39080.5	-1.2
17		36979.7		44	39152.5	39152.2	+0.3
18		37069.1		45	39222.6	39223.3	-0.7
19	37159.6	37157.9	+1.7	46	39293.9	39293.7	+0.2
20	37246.6	37246.0	+0.6	47	39362.8	39363.6	-0.8
21	37332.2	37333.3	-1.1	48	39433.4	39432.8	+0.6
22	37419.7	37420.0	-0.3	49	39501.9	39501.5	+0.4
23	37504.6	37506.0	-1.4	50	39569.0	39569.5	-0.5
24	37590.1	37591.3	-1.2	51	39636.0	39637.0	-1.0
25	37674.2	37675.9	-1.7	52	39704.3	39703.9	+0.4
26	37758.9	37759.8	-0.9	53	39769.6	39770.2	-0.6
27	37843.7	37843.0	+0.7	54	39836.6	39836.0	+0.6

TABLE III. Main spectroscopic constants for the ${}^{1}0_{u}^{+}(n {}^{1}P_{1})$ excited states of Zn₂ (*n*=4), Cd₂ (*n*=5), and Hg₂ (*n*=6). All in cm⁻¹ unless stated otherwise. Note: $\Delta R_{e} = R_{e}^{"} - R_{e}^{'}$.

	Zn ₂	Cd_2	Hg ₂
ω_0'		$100.20 \pm 0.25^{a,b}$	c
ω'_e	$122 \pm 10^{\circ}$	$100.50 \pm 0.25^{a,b}$ 101.2^{d}	79.0 ± 1.0^{r}
		$105.3 \pm 1.0^{\rm e}$	
$\omega'_e x'_e$	0.40 ± 0.04^{c}	$0.325\!\pm\!0.003^{a,b}$	$0.29556 \pm 2 \times 10^{-5f}$
		0.44 ± 0.03^{e}	
D_0'		$8643 \pm 15^{a,g}$	8236 ± 15^{h}
D'_{e}	$9010 \pm 200^{\circ}$	$8693 \pm 15^{a,i}$	$8280\!\pm\!15^{\rm h}$
-		9153 ^d	
		$8250 \pm 200^{\circ}$	
ΔR_e (Å)		1.04 ± 0.01^{a}	$0.84 \pm 0.01^{ m h}$
		$0.95 \pm 0.02^{c,e}$	
R'_{e} (Å)		$3.03 \pm 0.01^{a,j}$	2.8506^{f}
-		2.86 ^d	
ν_{00}		$35368.8 \pm 0.2^{a,b}$	46201.7 ^h
B'_e		0.0246 ^{a,k}	$0.020542 \pm 1 \times 10^{-6f}$

^aThis work, derived for the ²²⁶Cd₂ isotopomer.

^bThis work, Birge-Sponer plot.

^cReference [15].

^dThis work, *ab initio* calculation.

^eReference [16].

^fReference [60], derived for the (²⁰²Hg)₂ isotopomer.

^gThis work, Eq. (8).

^hReference [27], derived for the ⁴⁰¹Hg₂ isotopomer.

ⁱThis work, Eq. (9).

^jThis work, simulation of the ${}^{1}O_{u}^{+} \leftarrow X {}^{1}O_{g}^{+}$ excitation spectrum. ^kThis work, calculated as described in the caption of Fig. 3.

heaviest (²³²Cd₂) and the lightest (²¹²Cd₂) isotopomers, one can find that the ω'_e and $\omega'_e x'_e$ for all isotopomers differ by approximately 4.5% and 9%, respectively (see the insets in Fig. 4).

The D'_0 and D'_e of the ${}^10^+_u$ state can also be obtained from the following relationships:

$$D_0' = \nu_{\rm at} - \nu_{00} + D_0'', \qquad (8)$$

$$D'_{e} = D'_{0} + \frac{\omega'_{e}}{2} - \frac{\omega'_{e} x'_{e}}{4}, \qquad (9)$$

where $v_{at} = 43692.5 \text{ cm}^{-1}$ is the energy of the 5 ${}^{1}P_{1} - 5 {}^{1}S_{0}$ atomic transition [44], ground-state dissociation energy D''_{0} = 319.1 cm⁻¹ is taken from Ref. [13], and v_{00} = 35368.8 cm⁻¹ is the energy of the ${}^{1}0^{+}_{u}, v' = 0$ $\leftarrow X {}^{1}0^{+}_{g}, v'' = 0$ transition obtained from the extrapolation using the experimental value for the frequency of the v'= 19 $\leftarrow v'' = 0$ transition (in the 226 Cd₂ isotopomer), and ω'_{e} and $\omega'_{e}x'_{e}$ from BS analysis. Relationships (8) and (9) yielded $D'_{0} = 8643 \pm 15 \text{ cm}^{-1}$ and $D'_{e} = 8693 \pm 15 \text{ cm}^{-1}$, respectively, which significantly exceed the values obtained within anharmonic oscillator approximation. This suggests that the D'_{0} and D'_{e} determined with the help of the BS plot from Fig.



FIG. 5. The measured (full circles with error bars) and calculated for v' (our assignment, solid line), and $v' \pm 3$ (dotted lines) isotopic shifts Δv_{ij} [Eq. (7)] between different isotopic components in the ${}^{1}0_{u}^{+} \leftarrow X {}^{1}0_{g}^{+}$ excitation spectrum of Cd₂ shown in Fig. 2(a). For details see text.

4 are underestimated and Morse function cannot be used as a representation of the ${}^{1}0_{u}^{+}$ -state PE curve in a wide range of internuclear separations below the dissociation limit. The Morse representation is valid only in the region of v' probed in the experiment (which is based on the linearity of the BS plot) and can be expanded down to the vicinity of the bottom of the potential well.

In this region, the excited-state PE curve was also represented by turning-point pairs obtained quantum mechanically from an inverse perturbation approach (IPA) procedure [45,46] which was previously applied in this laboratory for modeling of the $B^{3}1(5^{3}P_{1})$ double-well excited-state potential in CdKr [47]. A computer program written by Pashov et al. [48] was employed for the calculation (for all details of the calculation method the reader is referred there). The basic idea of the IPA method is to start from a certain initially approximated potential $U_0(R)$ and to find a correction $\delta U(R)$, providing that the set of eigenvalues obtained by solving the Schrödinger equation with $U_0(R) + \delta U(R)$ would agree with the set of experimental energies in the least-squares-approximation sense. The potential $U_0(R)$ $+ \delta U(R)$ is treated then as a better approximation of the real PE curve and the whole procedure is repeated until certain convergence criterion is met. In our case, the $U_0(R)$ is that represented by the Morse function along with a set of experimental energies obtained directly from the excitation spectrum (see Table II). The points obtained from the calculation are shown in Fig. 6 (empty circles) while energies of the vibrational $v' \leftarrow v'' = 0$ transitions are listed in Table II. An agreement (within 0.1-1.8 cm⁻¹) between experimental energies and those obtained in the calculation was obtained. Figure 6 shows also the ${}^{1}0_{\mu}^{+}$ -state PE curve, which is represented by a Morse function with constants obtained in this work (see Table III) and is plotted only in the range 2.23-4.60 Å where the Morse representation is reliable. The IPA method applied here led to an improvement in representation of the excited-state potential. Figure 6 shows also a comparison between the result obtained from the experiment and



FIG. 6. PE curve for the ${}^{1}0_{u}^{+}(5 {}^{1}P_{1})$ state plotted using a Morse representation (thick solid line) with constants obtained in this work (see Table III). Results of the IPA procedure [open circles, the E(R) values are available from the authors (J.K.) upon request] and *ab initio* calculations (full circles) are also shown. A range of v' levels accessible in the excitation from the v''=0 ground-state level is indicated. The results are compared with a Morse representation (thin solid line) obtained by Rodriguez and Eden [15].

points (full circles) that were *ab initio* calculated (see Sec. II). The comparison shows that *ab initio* calculation produces the excited-state interatomic potential which has a somewhat deeper (approximately 5.3%) and shorter (approximately 3.9%) well depth and equilibrium internuclear separation, respectively.

Using data from the above analysis, we simulated the excitation spectrum recorded at the ${}^{1}0_{u}^{+} \leftarrow X {}^{1}0_{g}^{+}$ transition, employing a LEVEL 7.5 code of LeRoy [49]. This program solves the radial Schrödinger equation for bound levels and calculates the F-CF for transitions between rovibrational levels in the ground and excited states. The PE curve of the excited state was represented by turning-point pairs obtained from the IPA method. The wave function of the v'' level was generated using a Morse representation for the ground state [13] (for a more detailed description of the ground-state representation see Sec. V and Table IV). The result of the simulation (the "best fit") is shown in Fig. 2(b). The fit to the $v' \leftarrow v'' = 0$ progression includes also the isotopic composition of each vibrational component. The fit was obtained for $\Delta R_{e} = 1.04 \pm 0.01$ Å, which for $R_{e}'' = 4.07$ Å [13] yields $R'_{e}({}^{1}0''_{\mu}) = 3.03 \pm 0.01 \text{ Å}.$

V. THE FLUORESCENCE SPECTRUM

As mentioned in the Introduction, Rodriguez and Eden [15] and Tran and Eden [16] had previously reported on Condon internal diffraction (CID) patterns in Cd₂ fluorescence spectra. The spectra were interpreted as due to the bound-free radiative decays to the $X^{10}_{g}^{+}$ state from the non-selectively (v' = 20-24 and v' = 57-59) [15] and selectively (v' = 2, 3 and v' = 7, 8) [16] excited vibrational levels in the ${}^{10}_{u}^{+}$ excited state.

The v' assignments in the ${}^{1}0_{u}^{+}, v' \leftarrow X {}^{1}0_{g}^{+}, v'' = 0$ excitation spectrum reported here were additionally confirmed on

the basis of recorded fluorescence bands. The ²²⁶Cd₂ isotopomer in the v' = 39 and v' = 38 vibrational components was selectively excited and decayed to the repulsive part of the ground state, giving rise to the ${}^{1}O_{u}^{+}, v' = 39 \rightarrow X {}^{1}O_{g}^{+}$ and ${}^{1}O_{u}^{+}, v' = 38 \rightarrow X {}^{1}O_{g}^{+}$ bands, respectively. Figure 7(a) shows the gross structure of the resulting CID pattern. The band was recorded at relatively low resolution using a 40 cm⁻¹ MON slit width. The intense peak at the short-wavelength end of the band is interpreted as being due mainly to unresolved $v' = 38 \rightarrow v''$ bound-bound transitions to the closely spaced vibrational levels of the shallow ground-state well. The broad maximum at the long-wavelength end corresponds to the inner turning point in the potential of the bound-free part of the band, which will be described in detail below.

A. Bound-free transitions

To construct the repulsive part of the ground-state PE curve from the ${}^{1}0_{u}^{+}, v' = 39 \rightarrow X {}^{1}0_{g}^{+}$ and ${}^{1}0_{u}^{+}, v' = 38$ $\rightarrow X^{1}0_{g}^{+}$ [Fig. 7(a)] bound-free bands, we adopted the semiclassical RKR-like inversion method of LeRoy [50] and Child et al. [51]. This approach, which is complementary to the "exact" computational and fitting procedures, offers one advantage-it distinguishes between the "phase" and "amplitude" information in the experimental spectrum and shows how the positions of the intensity extrema are determined by the shape of the repulsive potential while the peak heights depend on the transition dipole moment $M_{z}(R)$. The experimental input data in this case were the energy values of the intensity extrema (maxima and minima) in the recorded fluorescence band. A polynomial fit was used to represent the positions of the experimental intensity extrema, while the inner and outer turning-point pairs for the ${}^{1}0_{\mu}^{+}$ -state potential were taken from an analysis of the excitation spectrum (for a result of the IPA method, see above). The resulting points representing the repulsive part of the $X^{1}0_{g}^{+}$ potential are shown in Fig. 8 (empty squares). To represent the part of the potential with an analytical function we chose a repulsive part of so-called Buckingham potential [52] which is repre-sented by a short-range Born-Mayer Ae^{-bR} function [53]. The unique values $A = 6.178 \times 10^{7}$ cm⁻¹ and b = 3.63 Å⁻¹ were found by overlapping the function with the points obtained by the inversion method (see Fig. 8, solid line). It has to be noted here that an attempt to represent the repulsive part by a Lennard-Jones (LJ) (n-6) function [23] (that was used in Hg₂ ground-potential representation [27]) basically failed; however, it allowed us to estimate a considerably low degree of the short-range Cd-Cd repulsion (n=4.45) as compared to the Hg₂ case (n = 6.21, see Table IV). Next, the profile of the bound-free band was simulated using the Born-Mayer potential. We used a BCONT 2.1 code [54,55], in which the PE curve of the ${}^{1}0_{u}^{+}$ state was, as before, represented by the turning-point pairs from the IPA procedure. The program made provision for the variation of the electronic dipole transition moment M_z with R. Theoretical values of $M_{\tau}^{2}(R)$ obtained in *ab initio* calculations [see Sec. II and curve (h) in the inset of Fig. 7, showing Ξ

	Zn ₂	Cd ₂	Hg ₂
ω_e''	25.9 ± 0.2^{a}	$\frac{23.0^{a}}{20.0^{l}, 19.2^{b}}$	$19.6 \pm 0.3^{\circ}$
$\omega''_e x''_e$	0.60 ± 0.05^{a}	0.40 ± 0.01^{a}	$0.26 \pm 0.05^{\circ}$
D''_e	279.1 ^a	330.5 ^a 290.0, ^d 287.3 ^b	380 ± 15^{c}
R_e'' (Å)	4.19 ^a 3.88, ^e 4.12 ^f	4.07 ^a 3.96, ^d 3.98 ^b	3.69 ± 0.01^{c} 3.63 ± 0.04^{g} 3.73^{h} , 3.94^{i}
n		$7.36^{j} \\ 4.45 {\pm} 0.02^{l,m}$	6.53 ^{c,k} 6.21±0.03 ^{c,n}
$egin{array}{c} A \\ b \ ({ m \AA}^{-1}) \\ C \end{array}$		$\begin{array}{c} (61.78 \pm 2.76) \times 10^{6 \ \text{l},\text{o}} \\ 3.63 \pm 0.01^{\text{l},\text{o}} \\ - 362.91 \pm 6.04^{\text{l},\text{o}} \end{array}$	
$C_6''/10^6 \;(\mathrm{cm}^{-1}\mathrm{\AA}^6)$	1.6624 ^p	1.99 ^q , 2.25 ^r 2.4529 ^e	1.4001 ^p
B''_e		0.0137 ^{l,s}	0.0123 ± 0.0001^{t}

TABLE IV. Main spectroscopic	constants for the 2	$X^{1}0_{g}^{+}(n^{-1}S_{0})$	ground states	of Zn_2 (<i>n</i>	n = 4), ($\operatorname{Cd}_2(n)$
=5), and Hg ₂ $(n=6)$. All in cm ⁻¹	unless stated other	rwise.				

^aReference [13].

^bThis work, *ab initio* calculation.

^cReference [27], derived for the ⁴⁰¹Hg₂ isotopomer.

^dReference [21].

^eReference [20].

^fReference [64].

^gReference [63].

^hReference [66].

ⁱReference [65].

^jThis work, calculated.

^kReference [27], calculated.

¹This work, derived for the ²²⁶Cd₂ isotopomer.

^mThis work, simulation of the ${}^{1}0_{u}^{+}$, $v' \rightarrow X {}^{1}0_{g}^{+}$ fluorescence spectrum, where v' = 38 or 39.

ⁿReference [27], simulation of the $G^{1}0_{u}^{+}$, $v' = 39 \rightarrow X^{1}0_{g}^{+}$ fluorescence spectrum.

^oThis work, simulation of the ${}^{1}0_{u}^{+}$, $v' \rightarrow X {}^{1}0_{e}^{+}$ fluorescence spectrum, where v' = 38 or 39.

^pSlater-Kirkwood formula [37] with correction of Ref. [38].

^qReference [61].

^rReference [62].

^sThis work, calculated as described in caption of Fig. 3.

^tReference [60], derived for the $(^{202}Hg)_2$ isotopomer.

 $\langle {}^{1}0_{\mu}^{+}|M_{z}(R)|X {}^{1}0_{\rho}^{+}\rangle$] were employed making possible the verification of experimental peak heights in the simulation. The calculations were performed for the ²²⁶Cd₂ isotopomer and rotationless structure in the upper and lower states [56]. The procedure used in the program also assumed a ν^3 dependence of the rate of photon emission (which is equivalent to the PM current) [43,59]. Since MON normally has a pass band with constant $\Delta \lambda$, it might be appropriate to multiply the F-CFs by ν^5 rather than ν^3 . This changes the relative intensities and shapes of the peaks in the structured continua, but does not change the positions of the maxima and minima which constituted the criterion for the "best fit." The result of the simulation is shown in Figs. 7(b) and 7(f). The repulsive part representation of the ground-state potential is shown in Fig. 8 together with the potential represented by a Morse function [13] (dotted line) showing the inadequacy of the latter in a representation of the short-range part of the potential. A comparison is also made with our result of *ab initio* calculations (full circles) and that of Yu and Dolg [21] (empty circles) showing a reasonable agreement.

B. Bound-bound transitions

To fully confirm the vibrational v' level from which the fluorescence was emitted, we recorded various parts of the fluorescence band at a higher resolution. The inset in Fig. 7 shows three traces of the band recorded at slit widths of (c) 30 cm^{-1} , (d) 20 cm^{-1} , and (e) 15 cm^{-1} , and results of a computer simulation are shown in trace (g). The simulation [49] of the bound-bound part of the fluorescence band close to the region of the excitation wavelength (2582.43 Å), shown in Fig. 7(g) employed the result obtained from the analysis of the excitation spectrum and bound-free part of the fluorescence spectrum. Because the ground-state Morse rep-



FIG. 7. (a) The total ${}^{1}0_{u}^{+}$, $v' = 38 \rightarrow X {}^{1}0_{g}^{+}$ fluorescence band recorded with a 40 cm⁻¹ MON slit width; $X_{eff} = 4$ mm, $p_{Ar} = 14$ atm, $T_{0} = 890$ K. The sharp peak at the short-wavelength end of the band is due to the $v' = 38 \rightarrow v''$ bound-bound transitions. (b) A computer simulation [54,55] of the bound-free part of the band showing the "best fit" obtained using a short-range $Ae^{-bR} + C$ Born-Mayer potential with $A = 6.178 \times 10^{7}$ cm⁻¹, b = 3.63 Å⁻¹, and C = -362.91 cm⁻¹ representing the $X {}^{1}0_{g}^{+}$ potential. The left inset shows the following: (c), (d), and (e) the short-wavelength part of the fluorescence band recorded with slit widths of 30, 20, and 15 cm⁻¹, respectively, (f) part of the simulation of the bound-free profile as in (b), (g) the simulation [49] of the bound-bound transitions (the individual F-CF corresponding to vibrational transitions—vertical bars—are represented by a Gauss convolution function representing the MON throughput with FWHM of 2 Å, i.e., approximately 30 cm⁻¹). The right inset (h) shows *ab initio* points calculated for the elements of the transition dipole moment $\langle 10_{u}^{+}|M_{z}(R)|X {}^{1}0_{e}^{+}\rangle$, and a region of R corresponding to the detected fluorescence spectrum is depicted.

resentation from Ref. [13] is reliable only from the bottom of the potential well up to the energy of the v''=3 (see the inset of Fig. 8), we therefore constructed a hybrid Morse-vdW potential to represent the total ground-state potential well up to the dissociation limit. In the repulsive part, it consisted of the Born-Mayer function with parameters obtained in the analysis of the bound-free part of the fluorescence spectrum, while in the vicinity of the R''_e and in the long-range region it was represented with the Morse function (with ω''_e and $\omega''_e x''_e$ from Ref. [13]) combined with the C''_6/R^6 dispersion func-



FIG. 8. PE curves for the $X^{10}_{g}(5^{1}S_{0})$ state plotted using the Morse representation [13] (dotted line) as well as the $Ae^{-bR}+C$ Born-Mayer potential with $A = 6.178 \times 10^{7}$ cm⁻¹, b = 3.63 Å⁻¹, and C = -362.91 cm⁻¹ (solid line); the repulsive part produced by the inversion procedure [53] (empty squares); points of our *ab initio* calculation (full circles); and the *ab initio* result of Yu and Dolg [21] (empty circles). The inset shows details of the bound part of the potential: all representations are as in the main figure, except a hybrid potential (solid line), i.e., the Born-Mayer combined with the Morse-vdW $[D''_{e}(1-e^{-\beta(R-R_{e})})^{2}-(1-e^{-(R/R_{c})^{12}})C''_{6}/R^{6}]$ potential plotted with D''_{e} = 330.5 cm⁻¹ [13], R''_{e} = 4.07 Å [13], C''_{6} = 2.46×10⁶ cm⁻¹ Å⁶ [23], and R_{c} = 9.2 Å determined in this work. The position of the v'' = 3 vibrational level [13] is shown.

tion (with C''_6 obtained using the Slater-Kirkwood formula [37] with a correction of Cambi *et al.* [23,38], see Table IV). The two functions were smoothly joined in the so-called Morse-vdW potential [23] using an $(1 - e^{-(R/R_c)^{12}})$ term with $R_c = 9.2$ Å. From the simulation [Fig. 7(g)] it became clear that the first six peaks and part of the seventh peak at the short-wavelength end of the fluorescence band were due to unresolved bound-bound transitions, while the remaining peaks were due to bound-free transitions. All the 39 maxima present in the CID pattern were identified in the traces in Fig. 7, confirming the v' assignments obtained from the analysis of the isotopic structure in the excitation spectrum. Moreover, the $\Delta v' = \pm 3$ error margin that was concluded from the isotopic-shift analysis (see Sec. IV) was eliminated. The simulation of both ${}^{1}O_{u}^{+}, v' = 39 \rightarrow X {}^{1}O_{g}^{+}$ and ${}^{1}O_{u}^{+}, v' = 38$ $\rightarrow X^{1}0_{\rho}^{+}$ (Fig. 7) bands indicates that the v' assignments were determined from fluorescence spectra accurately, without any uncertainty. The ground-state spectral characteristics of Cd₂ are collected in Table IV and compared with results of other experiments and *ab initio* calculations.

VI. CONCLUSIONS

The ${}^{1}0_{u}^{+}(5 {}^{1}P_{1})-X {}^{1}0_{g}^{+}$ excitation and fluorescence spectra of Cd₂ molecules were studied in a continuous free-jet supersonic expansion beam crossed with a pulsed dye-laser beam. A well-resolved vibrational structure in the ${}^{1}0_{u}^{+}, v' \leftarrow X {}^{1}0_{g}^{+}, v''=0$ excitation spectrum was recorded, as well as the isotopic structures of the individual vibrational components. An isotope shift analysis produced v' assignments. Vibrational characteristics $\omega_{e}'=100.50\pm0.25 \text{ cm}^{-1}$ and $\omega_{e}'x_{e}'=0.325\pm0.003 \text{ cm}^{-1}$, as well as dissociation energy $D_{0}'=8643\pm15 \text{ cm}^{-1}$, well depth $D_{e}'=8693\pm15 \text{ cm}^{-1}$, and the difference between equilibrium internuclear separations $\Delta R_{e}=1.04\pm0.01$ Å for the ${}^{226}\text{Cd}_{2}$ isotopomer were determined by modeling the excitation spectrum. The ${}^{1}0_{u}^{+}$ state potential-energy curve was obtained numerically using an inverse perturbation approach (IPA) procedure. The analysis

of the Condon internal diffraction patterns in the ${}^{1}0_{u}^{+}, v'$ $=38 \rightarrow X^{1}0_{g}^{+}$ and 10_{u}^{+} , $v'=39 \rightarrow X^{1}0_{g}^{+}$ fluorescence bands, emitted upon selective excitation of the v' = 38 and v' = 39vibrational components, respectively, improved the v' assignments of the peaks in the excitation spectrum. Simulation of the excitation spectrum yielded Morse or numerical representation of the ${}^{1}0_{\mu}^{+}$ -state PE curve in the 2.5–4.5 Å region of internuclear separations. Simulation of the boundfree part of the fluorescence band showed that a short-range $Ae^{-\bar{b}R}$ Born-Mayer function of the Buckingham-type potential with $A = 6.178 \times 10^7$ cm⁻¹ and b = 3.63 Å⁻¹ is a good representation of the ground state potential above the dissociation limit. Below the dissociation limit the ground-state potential could be represented by a hybrid potential consisted of the Born-Mayer and Morse-vdW combined functions. An analysis of the excitation spectrum yielded molecular constants that are compared in Tables III and IV with those obtained from other experiments [15,16] and *ab initio* calculations. Quasirelativistic valence ab initio calculations on the potential-energy curves for the investigated states were performed with the total 40 correlated electrons. In the calculations, the Cd atom was considered as a 20-valence electron system whereas the Cd²⁰⁺ core was replaced by an energyconsistent pseudopotential. The results of the simulation of the bound-free part of the fluorescence spectrum as well as ab initio calculations and their comparison, especially with the recent result of Yu and Dolg [21], suggest that a covalent admixture is present in the cadmium dimer ground-state vdW bonding. However, the conclusion needs future experimental confirmation.

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