Potential energy curves and transition moments for the excimer states $0_u^+ (^3P_1)$ and $1_u (^3P_2)$ of Ar$_2$

Matti Selg

Institute of Physics of the University of Tartu, Riia 142, 51014 Tartu, Estonia

Abstract

Exactly solvable reference potentials of several smoothly joined Morse-type components were constructed for the lowest two excimer states of Ar$_2$ molecule. The parameters of the potentials have been ascertained by fitting to the experimental data, and they are reliable in a wide range of nuclear separations ($r \geq 1.9$ Å). A large number of quantum mechanical Franck-Condon factors for the $0_u^+ \rightarrow 0_g^+$ and $1_u \rightarrow 0_g^+$ transitions have been calculated and compared with the observed spectroscopic features. The fitting procedure also involved dipole transition moments, which have been adjusted to the known radiative lifetimes of the vibrational levels. The resulting potential energy curves accurately reproduce the first and the second emission continua of Ar$_2^*$ as well as the oscillatory spectrum related to their inner turning point region. The numbering and the positions of the vibrational levels reported by Herman et al. [P. R. Herman, P. E. LaRocque, and B. P. Stoicheff, J. Chem. Phys. 89, 4535 (1988)] have been confirmed. The calculated spectroscopic parameters, $\omega_e = 296.26$ cm$^{-1}$, $D_e = 6128.3$ cm$^{-1}$ for the $0_u^+$ state, and $\omega_e = 287.30$ cm$^{-1}$, $D_e = 5929.6$ cm$^{-1}$ for the $1_u$ state, are consistent with previous estimations. Separation between the minima of the potential wells at $R_e = 2.3893$ Å was found to be 50.60 meV, compared with 75.24 meV splitting in the separated-atom limit.
I. INTRODUCTION

Rare gases (RG) are important laser media in the vacuum ultraviolet (VUV) spectral region [1, 2], and this is one of the reasons for the undying interest in these chemically inactive species. Normally, they are almost atomic gases, because electronically unexcited RG dimers are only weakly bound (except radioactive Rn\textsubscript{2} with dissociation energy of about 400 K [3]). In contrast to this, the electronically excited RG dimers (excimers) in their lowest states \(1_u^+\) and \(0_u^+\) are strongly bound. These excimers can be created with the help of various excitation sources (charged particle beams, synchrotron radiation, etc.), and their decay produces photons in the VUV region, forming two intense continua observed long ago for all RGs (except Rn) [4, 5, 6, 7, 8] (see also [9, 10] for the recent Ne and He data).

A vast literature exists on the RG dimers in their ground electronic state [3, 11, 12, 13, 14, 15, 16, 17, 18], because they are good prototypes for studying van der Waals interactions. At the same time, there is still a lack of knowledge about the RG excimer states, which are of crucial importance for the development of efficient light sources in the VUV region [10, 19, 20, 21, 22, 23]. Of special interest in this context are the heavier excimers for which the laser emission has been reported [1, 2]. The observed laser effect is related to the so-called second continua, broad structureless emission bands with maxima at 126, 146 and 172 nm for Ar\textsubscript{2}*, Kr\textsubscript{2}*, and Xe\textsubscript{2}*, respectively. They correspond to transitions from the vibrationally relaxed \(1_u\) and \(0_u^+\) states to the repulsive part of the ground electronic state \(0_g^+\), in contrast to the so-called first continua originating from the highest vibrational levels of the \(0_u^+\) excimer state, and therefore being spectrally close to the atomic \(3P_1 \rightarrow 1S_0\) resonance lines. The first continuum is related to the excimers’ classical outer turning point region, while the weak oscillatory emission from the region of their inner turning points has also been observed under selective synchrotron radiation excitation [24].

All these important spectroscopic features can be uniformly treated [25, 26], but to this end, one needs reliable potential energy curves (PECs) and coordinate dependencies of the related transition moments, as well as a reasonable model to describe vibrational relaxation of the excimers. In this paper, we concentrate on the first two issues, while the relaxation dynamics and the time-dependent emission spectra will be studied in a separate paper [27]. Valuable information on the energetic position, absolute numbering and radiative lifetimes of the higher vibrational levels for all heavier RG excimers has been obtained in a series
of supersonic jet expansion experiments [28, 29, 30, 31], using tunable VUV radiation to produce high-resolution fluorescence excitation spectra. Unfortunately, these high-quality reference data concern only a narrow range of vibrational levels near the dissociation limit, and one cannot construct reliable PECs for RG excimers solely on this basis. Various ab initio and semi-empirical potentials are available [32, 33, 34, 35, 36, 37, 38], which satisfactorily reproduce some of the characteristic spectroscopic features, but not the whole variety of available experimental data. Apart from imperfections of the PECs of the excimer states, the discrepancies between theoretical and experimental spectra may be caused by inaccuracies of the ground state potentials in the short distance range.

Thus, the spectroscopic properties of RG dimers certainly need further investigation. This is the motivation for the present study, the main goal of which is to construct accurate reference potentials of relatively simple analytic form, by directly fitting their parameters to the observed data, and taking account of the relevant theoretical considerations. In principle, the approach that will be described below can be applied to any RG dimers, since they have much in common. For several reasons, however, only Ar$_2$ molecules are under examination in this paper. First, compared with Xe and Kr, the effects of spin-orbit coupling are much less pronounced in Ar, which makes the theoretical analysis more simple and, hopefully, more adequate. Second, a sufficient amount of good-quality experimental data are available for Ar gas, which, again, is an advantage compared with Xe and Kr. Third, there is a practical point of special interest in Ar$_2^*$ excimers, as they produce the highest energy photons (9.8 eV) for the potential laser applications, which is the field of great interest and permanent development [39, 40]. It therefore seems reasonable to test the method on Ar$_2$ molecules, leaving more complex cases for the future analysis.

The reference potential approach to different spectral problems has been described in detail elsewhere (see, e.g., [25, 41] and references therein). In this paper, we are going to construct smooth multi-component exactly solvable reference potentials for the lowest excimer states $1_u$ and $0_u^+$, and for the ground electronic state $0_g^+$ of the Ar$_2$ molecule. These approximate PECs should be realistic in a wide range of nuclear separations related to the observed spectroscopic features. To achieve this goal, fully quantum mechanical calculations of bound-bound and bound-free Franck-Condon factors for $1_u \rightarrow 0_g^+$ and $0_u^+ \rightarrow 0_g^+$ transitions have been performed. The procedure has to be repeated many times, varying the parameters of the PECs and the transition moments. In this way, step by step, the calculated energy
levels and their radiative lifetimes, as well as the intensity patterns of Franck-Condon factors, can be fitted to the available experimental data.

The paper is organized as follows. In Section II, a short overview of the theoretical background of the method is given, specific properties of the reference potentials for the $0_g^+$, $0_u^+$ and $1_u$ electronic states of Ar$_2$ are described (in sub-sections A, B, and C, respectively), and the details of the fitting procedure are explained. Section III is devoted to demonstrating the calculated Franck-Condon factors, transition probabilities and radiative lifetimes for the vibrational levels of the $0_u^+$ and $1_u$ states. Finally, a brief discussion of the obtained results and future prospects of the research are given in Section IV, which concludes the paper.

II. EXACTLY SOLVABLE MULTI-COMPONENT REFERENCE POTENTIALS

At first sight, the reference potential approach we are going to adopt may seem naive and unjustified. However, the solution to a problem always depends on the context. Modern spectroscopic analysis often involves many thousand items of high resolution input data, but unfortunately, such detailed information is not yet available neither for the ground state of Ar$_2$ molecule nor for the excimer states $1_u$ and $0_u^+$. Indeed, the scattering data for these species are almost lacking. Moreover, even the total number of the bound states is not conclusively established, and only a narrow range of discrete levels has been accurately ascertained for the excimer states [30], while their absolute numbering still needs to be confirmed. Under these circumstances, there is no chance to deduce the ”real” PECs directly from the experimental data. One can only take some steps towards this goal by combining the available experimental data with the relevant theoretical results. In this context, the simple but mathematically rigorous approach in question has proven to be quite useful.

To begin with the analysis, let us recall another important peculiarity of the system under study. Namely, for all RGs, there is a big difference (about 1.4 Å in the case of Ar$_2$) between the minima of the tiny potential well of the ground state and those for the excimer states. It means that bound-free transitions to the repulsive wall of the ground state PEC are responsible for the major part of the observed fluorescence spectra. Of course, as we demonstrate, bound-bound transitions are also very important to reveal the details of the first emission continuum. Unfortunately, this fine structure, which should contain tens of spectral lines in the range of less than 0.1 eV width (compared with more than 4.5 eV width
of the overall spectrum), has not yet been detected experimentally. Moreover, the spectral resolution in fluorescence experiments on Ar and other RGs is typically $\sim 10$ meV. Therefore, at the present level of our knowledge, one should not put too much effort into deducing the PECs that would reproduce the observed (relatively few) level positions with the utmost accuracy. Formally, one can always achieve this specific goal, but this does not guarantee the reliability of the potentials in the major part of the domain. Indeed, as is well known, even the full knowledge of the discrete energy spectrum combined with the full scattering information is insufficient to uniquely determine the potential [42].

In view of the above, we set the following criteria to the quality of the reference potentials for the Ar$_2^*$ excimer states: 1) these PECs should reproduce the observed bound-bound transition energies [30] with $\sim 1$ meV accuracy; 2) they should reproduce all details of the fluorescence spectra in the range from about 7 to 11.63 eV with $\sim 10$ meV accuracy. To achieve these goals, we use a fitting method which is based on repeated and accurate calculation of the Franck-Condon factors. Naturally, this strictly quantum mechanical procedure presumes highly efficient solution of the Schrödinger equation, because this elementary act has to be performed many million times within a reasonable time scale. For this reason, we try to adopt an analytic approach of calculating the energy eigenfunctions, which indirectly means that we have to construct exactly solvable approximants (reference potentials) to the "real" PECs. If one sets a "physical constraint", requiring continuity of the potential and its first derivative in the whole physical domain, the number of suitable options becomes quite limited. Certainly one of the best choices is to compose a reference potential of several Morse-type [43] pieces

$$V(r) = V_k + D_k \left[ \exp(-\alpha_k(r - R_k)) - 1 \right]^2, \quad r \in (0, \infty), \quad (1)$$

where $V_k, D_k, \alpha_k$ and $R_k$ are real (not definitely positive!) constants, and the subscript $k = 0, 1, 2...$ labels different components smoothly joined at the boundary points $X_{k+1}$.

As is well known, the classical Morse potential belongs to the family of shape invariant potentials [44], and its energy eigenvalue problem can be solved with the help of solely algebraic techniques. The shape invariance is lost, if there are several analytically different components, as assumed in Eq. (1). Consequently, the discrete energy levels of such multi-component potentials cannot be given in an explicit analytic form. With some concession, we can still preserve the term "exactly solvable" for this kind of piece-wise potentials, because
the two linearly independent solutions of the related Schrödinger equation can be always found analytically to any desired accuracy. Indeed, introducing a dimensionless variable
\[ y_k \equiv 2a_k \exp(-\alpha_k(r-R_k)), \]
the Schrödinger equation for a Morse-type PEC can be converted into a confluent hypergeometric form [45]
\[
\frac{d^2G(a_k, \mu_k; y_k)}{dy_k^2} + (2\mu_k + 1 - y_k) \frac{dG(a_k, \mu_k; y_k)}{dy_k} + (a_k - \mu_k - 1/2)G(a_k, \mu_k; y_k) = 0. \tag{2}
\]

Here \( a_k \equiv \sqrt{D_k/C/\alpha_k}, \) \( \mu_k \equiv \sqrt{(V_k+D_k-E)/C}, \) and the solutions of the Schrödinger equation read (up to normalization)
\[
\Psi = \exp(-y_k/2)y_k^{\mu_k}G(a_k, \mu_k; y_k).
\]
Note that the parameters \( a_k, \mu_k \) and the coordinate \( y_k \) may be imaginary, if \( D_k < 0 \) or the total energy \( E > V_k + D_k. \)

There are several possibilities to construct the fundamental system of solutions for Eq. (2) (see [45], Chapter 6, for a thorough overview). For example, one can make use of the special solutions
\[
G_1 = \Phi(-a_k + \mu_k + 1/2, 2\mu_k + 1; y_k), \quad G_2 = y_k^{-2\mu_k}\Phi(-a_k - \mu_k + 1/2, -2\mu_k + 1; y_k), \tag{3}
\]
where the symbols
\[
\Phi(a, c; x) \equiv 1 + \frac{a \cdot x}{1! \cdot c} + \frac{a(a + 1) \cdot x^2}{2! \cdot c(c + 1)} + \ldots \tag{4}
\]
denote confluent hypergeometric functions. Correspondingly, the two linearly independent solutions of the original Schrödinger equation read
\[
\Psi_{k1} = y_k^{\mu_k}S(a_k, \mu_k; y_k), \quad \Psi_{k2} = y_k^{-\mu_k}S(a_k, -\mu_k; y_k), \tag{5}
\]
where we have introduced another very useful function
\[
S(a, c; x) \equiv \exp(-x/2)\Phi(-a+c+1/2, 2c+1; x), \tag{6}
\]
which can be evaluated as follows [46]:
\[
S(a, c; x) = \sum_{n=0}^{\infty} B_n, \quad B_0 = 1, \quad B_1 = -\frac{ax}{2c+1}, \tag{7}
\]
\[ B_n = \frac{x}{n(2c+n)}(-aB_{n-1} + \frac{x}{4}B_{n-2}), \quad n = 2, 3, \ldots \]

From Eqs. (5) to (7) one can infer that \( \Psi_{k1} \) and \( \Psi_{k2} \) are always complex conjugates, if \( E > V_k + D_k. \)
A. Four-component reference potential for the ground state of Ar$_2$

After the brief theoretical introduction, let us try to put the ideas into practice. Our fitting procedure does not actually involve the parameters of the ground state, but only those of the excimer states $1_u$ and $0_u^+$. In other words, the PEC for the ground state is assumed to be fixed. Nevertheless, in order to solve the whole quantum mechanical problem exactly, we have to construct an exactly solvable (in the above-mentioned sense) reference potential for the ground state as well. Of course, such a constraint is technical rather than conceptual. The Schrödinger equation can be always solved numerically, but in the present context the main problem is how to fix a sufficiently realistic PEC. The shape of the ground state potential for Ar$_2$ is accurately known in the intermediate and long-distance range, but the knowledge about its repulsive short-distance part is rather ambiguous. As mentioned, this region is very important to interpret the observed spectroscopic features, thus our aim is to describe the repulsive wall as adequately as possible.

The resulting reference PEC for Ar$_2$ is shown in Fig. 1, and its parameters are given in Table 1. All four components have the simple analytic form of Eq. (1), and their parameters have been ascertained from the least squares fit to the ab initio CCSD(T) daug-cc-pV5Z-33211 potential by Fernández and Koch [47]. This particular PEC has been preferred, because this is the only work to date where both the ground state and the excimer state ($0_u^+$) potentials have been calculated on the same theoretical basis. These PECs nicely reproduce the observed spectra related to the excimers’ inner turning point region [24], which is a strong argument for their reliability at short distances. As can be seen in Figs. 1 and 2, the ground state PEC by Fernández and Koch is in good agreement with the other available ab initio potentials [18, 48]. The reference potential for Ar$_2$ is almost indistinguishable from the original PEC on the scale used in these figures. Therefore, it is expected to be reliable enough for our purposes.

Now, let us have a look at the structure of this reference PEC. The two most internal components ($r \leq X_1$ and $r \in [X_1, X_2]$, respectively) represent the so-called pseudo-Morse (PM) potentials [23, 41] smoothly joined at the boundary point $X_1$. Their important peculiarity is that the parameters $D_k$ and $\alpha_k$ ($k = 0, 1$) are not independent, but $D_k = \frac{1}{4} C \alpha_k^2$. It means that the tiny potential well is just of the limit depth to entirely lose the discrete energy spectrum. Since $a_k = 1/2$, and the pseudo-Morse approximation is used only in the
region where \( E > V_k + D_k \), the two special solutions \( \Psi_{k1} \) and \( \Psi_{k2} \) of the Schrödinger equation are complex conjugates. According to Eqs. (5) to (7),

\[
\Psi_{k1} = y_k e^{iB_k(y_k)} e^{-i\alpha_k \beta_k (r - r_k)},
\]

where

\[
A_k(y_k) e^{iB_k(y_k)} \equiv 1 - \frac{y_k/4}{i\beta_k + 1/2} + \frac{(y_k/4)^2}{(i\beta_k + 1/2) 1!} \left( 1 - \frac{y_k/4}{i\beta_k + 3/2} \right) + \frac{(y_k/4)^4}{(i\beta_k + 1/2) (i\beta_k + 3/2) 2!} \left( 1 - \frac{y_k/4}{i\beta_k + 5/2} \right) + \ldots,
\]

and, consequently, the general solution reads

\[
\Psi_k(r) = N_k A_k(y_k) \cos [B_k(y_k) + \varphi_k - \alpha_k \beta_k r], \quad k = 0, 1.
\]

Here \( \beta_k \equiv |\mu_k| \), while the normalization factor \( N_k \) and the phase constant \( \varphi_k \) should be determined from the continuity requirements of the wave function and its derivative.

The phase constant \( \varphi_0 \) for the most internal PM component can be always (in most cases quite easily) ascertained analytically [41], taking account of the physical boundary condition \( \Psi \to 0 \) as \( r \to 0 \). The next phase constant \( \varphi_1 \) can then be determined from the boundary condition \( \frac{\Psi_1'(X_1)}{\Psi_0'(X_1)} = \frac{\Psi_1'(X_1)}{\Psi_0'(X_1)} \). In all cases analyzed in this paper the wave function’s logarithmic derivative can be expressed in the form

\[
\frac{\Psi_k'(r)}{\Psi_k(r)} = \alpha_k \left[ R_k(r) + \frac{S_k(r) \tan \varphi_k + T_k(r)}{U_k(r) \tan \varphi_k + W_k(r)} \right]
\]

where \( R_k, S_k, T_k, U_k \) and \( W_k \) are some characteristic functions that do not depend on phase constants. Thus, if \( \varphi_0 \) is known, \( \varphi_1 \) can be easily determined.

The region \( r \in [X_2, X_3] \) (including the minimum of the PEC) is approximated by an ordinary Morse (OM) potential \( (k = 2) \). Again, since the energy range \( E < V_2 + D_2 \) is out of interest, the special solutions \( \Psi_{21} \) and \( \Psi_{22} \) are complex conjugates, and the general solution of the Schrödinger equation becomes

\[
\Psi_2(r) = N_2 \left[ C_2(r) \tan \varphi_2 + D_2(r) \right],
\]

where

\[
C_2(r) \equiv \Re \left[ S(a_2, i\beta_2; y_2) \sin(k_2r) \right] - \Im \left[ S(a_2, i\beta_2; y_2) \cos(k_2r) \right],
\]

\[
D_2(r) \equiv \Re \left[ S(a_2, i\beta_2; y_2) \cos(k_2r) \right] + \Im \left[ S(a_2, i\beta_2; y_2) \sin(k_2r) \right],
\]
\[ k_2 \equiv \alpha_2 \beta_2, \text{ and } \beta_2 \equiv |\mu_2| \]. To ascertain the phase constant \( \varphi_2 \), one uses Eq. (11) and applies the boundary condition \( \frac{\Psi_3'(X_2)}{\Psi_2'(X_2)} = \frac{\Psi_3'(X_2)}{\Psi_2'(X_2)} \).

The most external region \( r \geq X_3 \) is approximated by a reversed Morse (RM) potential with a negative "dissociation energy" \( D_3 \). This might seem unphysical, because there is actually no hump on the original PEC. However, since the hump of the reference PEC is very small and located in the long-distance range (see Table 1) where \( V(r) \approx 0 \), this artificial effect is nearly negligible for spectroscopic applications, while the analytic treatment remains as simple as in previously studied cases. Of course, one can introduce more such components and gradually shift the maximum to an arbitrarily long distance (in principle, to infinity), thus practically eliminating the artificial barrier. In this paper, this physically motivated but tedious procedure has not been undertaken, because the desired quality of the PECs (see the criteria set in Section II) can already be achieved with the help of only 3-4 components.

A thorough analysis of the bound-states region \( E < V_3 + D_3 = 0 \) has been given elsewhere [49]. For the scattering states \( (E > 0) \), the wave function reads

\[ \Psi_3(r) = \frac{2C_3(r)}{\sqrt{\tan^2 \varphi_3 + 1}} \left\{ \cos [D_3(r) - kr] - \tan \varphi_3 \cdot \sin [D_3(r) - kr] \right\}, \]  

where \( C_3(r) \exp[iD_3(r)] \equiv S(i\alpha_3, i\beta_3; ix_3), \beta_3 \equiv |\mu_3|, x_3 \equiv |y_3|, \) and \( k \equiv \alpha_3 \beta_3 = \sqrt{E/C} \). Since \( C_3(r) \to 1 \) and \( D_3(r) \to 0 \) as \( r \to \infty \), \( \Psi_3(r) \) asymptotically approaches the free-wave form, \( \Psi_3(r) \approx 2 \cos(\varphi_3 - kr) \). Consequently, the main spectral characteristic of the scattering states, the phase shift, reads \( \delta(k) = (n + 1/2)\pi - \varphi_3 \), where \( n \) is an integer.

To ensure the correct energy normalization, Eq. (13) has to be multiplied by the factor \( F = \left( \frac{4\pi \sqrt{EC}}{1} \right)^{-1/2} \) [50]. As previously, to ascertain the phase constant \( \varphi_3 \), one has to suitably adjust Eq. (11) and apply the boundary condition \( \frac{\Psi_3'(X_3)}{\Psi_2'(X_3)} = \frac{\Psi_3'(X_3)}{\Psi_2'(X_3)} \). Thereafter, one can fix the normalization factors \( N_2, N_1 \) and \( N_0 \), using the continuity conditions for the components of the wave function

\[ \Psi_3(X_3) = \Psi_2(X_3), \Psi_2(X_2) = \Psi_1(X_2), \Psi_1(X_1) = \Psi_0(X_1). \]

Thus we have explained all details of calculating the stationary wave functions for an exactly solvable multi-component reference potential. The described scheme remains the same, independent of how many analytically different components one introduces. In view of the incomplete knowledge about the real PEC for Ar\(_2\), including just four smoothly joined
Morse-type pieces seems quite optimal. In fact, the full discrete energy spectrum \( E_n < 0 \) \((n = 0 \pm 6)\) can be accurately ascertained with the help of only two components (OM + RM), because the region \( r < X_2 = 3.35 \) Å becomes practically negligible for these calculations. Determining the energy levels therefore reduces to a very simple zero-finding problem for a function, which is uniquely determined by the physical boundary conditions \( \Psi_2(E, r) \rightarrow 0 \) as \( r \rightarrow 0 \) and \( \Psi_3(E, r) \rightarrow 0 \) as \( r \rightarrow \infty \), complemented with the condition
\[
\frac{\Psi_2'(E, r)}{\Psi_2(E, r)} = \frac{\Psi_3'(E, r)}{\Psi_3(E, r)}
\]
for an arbitrary \( r > X_2 \) (e.g., \( r = X_3 \)). These three conditions can be fulfilled simultaneously only for the true energy eigenvalues, i.e., if \( E = E_n \).

In Fig. 1 one can see little discrepancies between the original PEC and its approximant, which could be easily reduced by adding more components. An important point to discuss in this context is the physically correct long-range behavior of the potential. Indeed, apart from the artificial potential barrier, RM approximation seems to be absolutely incompatible with the attractive inverse power series coordinate dependence, which is expected at long distances. However, in the framework of the proposed approach, the "unphysical" nature of the RM approximation and the discrepancies mentioned are not substantial. First, as can be seen in Table 1, the calculated vibrational levels for the reference PEC fit with the observed ones [30, 51] even better than those of the original potential. Thus, adding more components to the potential is not motivated. Second, in a wide range of actual interest the RM approximation does not contradict to the inverse power series expansion (see the inset of Fig. 1). Therefore, since the described approach is reliable enough, and provides simple analytic solution to the problem, it has been used in the long distance region as well.

As mentioned, the parameters of the ground state reference potential were kept unchanged. A large number of scattering \((E > 0)\) wave functions for this PEC have been calculated, along with the wave functions of the bound states. These eigenfunctions are needed as a basis for further calculations, and this basis should be sufficiently complete to accurately reveal all details of the Franck-Condon factors for the vibrational levels of the excimer states.

### B. Reference potential for the \( 0^+_u \) state of Ar\(_2^+\)

Construction of the reference potentials for the excimer states can be performed in the manner described in the previous subsection. The main difference is that the parameters
of the components are now treated as variables to be fitted to the experimental data. In addition, the \textit{ab initio} CCSR(T) daug-cc-pV5Z potential for the \(0_u^+\) state in the range \(r < 2.7\ \text{Å}\) has also been used as an input for the fitting procedure. Therefore, in this region (including the minimum at 2.3893 Å) the reference potential practically does not differ from the PEC calculated by Fernández and Koch.

As previously, the reference potential was built up of several smoothly joined Morse-type pieces. Since spectroscopic applications are related to the excimers’ bound states, the short-distance region \((r < 2\ \text{Å})\) is of less interest, and therefore, the reference PEC constructed for the \(0_u^+\) state does not include any PM components. Thus, the resulting curve shown in Figs. 2 and 3 has only three constituents with parameters given in Table 2. The region \(r \leq X_1\) was approximated by an OM potential, and two RM components \((r \in [X_1, X_2] and r \geq X_2, \) respectively), have been introduced for the long-distance range where spin-orbit coupling becomes important. Note that we cannot use the \textit{ab initio} PEC by Fernández and Koch for this range, because spin-orbit coupling was ignored in their calculations.

As mentioned, the PM component remained nearly unchanged, while the RM components have been largely varied, preserving the continuity of the potential and its derivative, and trying to achieve a good fit with the experimental data. First, for any intermediate reference PEC, the energy eigenvalue problem has been solved. As explained in the end of the previous sub-section, the discrete energy levels can be always found as the zeros of a characteristic function, which is uniquely determined by the physical boundary conditions and the continuity requirements (see, e.g., [49] and references therein for more details). Thereafter, the Franck-Condon factors for all vibrational levels were calculated and integrated over the full energy range. The results have been compared with the corresponding experimental data. If needed, the parameters of the reference PEC have been slightly changed and the whole procedure has been repeated until the desired quality of the fit was achieved.

Naturally, the correct PEC should reproduce the second continuum and the real dissociation limit \((E_a = 11.623592\ \text{eV for the atomic}^{3}\text{P}_1 \text{ level}[52]).\) In addition, the fitting procedure involved the observed level positions [30] and the intensity patterns from the excimers’ inner turning point region [24]. Unfortunately, only rough estimations for the important spectroscopic constant \(\omega_e\) of the \(0_u^+\) state are available (see, e.g., [30]), but it has to be close to the values reported for the \(1_u\) state \((\omega_e = 293 \pm 4\ \text{cm}^{-1}[53], \omega_e = 299 \pm 3\ \text{cm}^{-1}[54])\) and for the \(2\Sigma_{1/2u}^+\) state of \(\text{Ar}_2^+\) \((\omega_e = 307 \pm 0.4\ \text{cm}^{-1}[55])\). Finally, one has to
take account of the known radiative lifetime for the $0^+_u$ constituent of the second continuum, $\tau = 4.20 \pm 0.13$ ns \cite{50}. To achieve agreement with this value, the transition moment given by Fernández and Koch has been corrected in the range $r < 3$ Å (see the inset in Fig. 2).

Table 2 and Figs. 3 and 4 demonstrate the obvious success of the described procedure.

C. Reference potential for the $1_u$ state and $1_u \rightarrow 0^+_g$ transition moment

The reference potential constructed for the $1_u$ state looks similar to the $0^+_u$ PEC just described (see Fig. 2), although the fitting procedure was slightly different. This time, no \textit{ab initio} PECs can be used for comparison, but on the other hand, a lot more experimental data are available. In addition to the level positions and their absolute numbering in the range $v' = 23 \div 31$ \cite{30, 57}, the radiative lifetimes for $v' = 0$ ($\tau = 3.2 \pm 0.3$ µs \cite{50}) and $v' = 24 \div 30$ \cite{31} have been reported, the spectroscopic constant $\omega_e$ is known \cite{53, 54}, etc.

As for the $0^+_u$ state, a reference potential of three components (OM + RM + RM) has been constructed, but this time all parameters have been varied, except the equilibrium separation $R_e = 2.3893$ Å \cite{47}, which was kept fixed. The parameters of the PEC and the transition moment can be fitted independently, since the radiative lifetimes do not depend on the position of the levels. In its essence, the fitting procedure was the same as described in the previous subsection. As can be seen from Table 3 and Figs. 3 and 5, a good fit with the experimental data has been achieved for the $1_u$ excimer state as well. The transition moment curve shown in the inset of Fig. 2 is similar to that reported by Madej and Stoicheff \cite{31}, but it falls to zero ($1_u \rightarrow 0^+_g$ transition is forbidden in the separated-atom limit) more slowly as $r \rightarrow \infty$.

III. FRANCK-CONDON FACTORS AND RADIATIVE LIFETIMES

Calculation of Franck-Condon factors for the fixed pair of PECs and known transition moment is a routine but rather time consuming task that has to be performed very accurately. In the present case, even more computational work is required because this demanding procedure is used for fitting purposes. Fortunately, there are some possibilities to reduce the amount of computations. First, since the ground state reference potential is fixed, one has to calculate the related wave functions only once. Second, for any reference PEC under
examination, one has to solve the Schrödinger equation only at predefined points, e.g., at
the abscissas of the relevant Gaussian quadrature formula.

Thus, 640 wave functions for the ground state reference PEC have been calculated in
the range \( E \in [0, 4.7 \text{ eV}] \) with a variable energy step from 0.001 to 20 meV. Few examples
of these eigenfunctions, all having the asymptotic form \( \Psi(r) \approx 2 \cos(\varphi_3 - kr) \) according to
Eq. (13), can be seen in Fig. 6. Of special interest might be the top graph in this figure,
because it illustrates some fundamental findings of the quantum scattering theory at very low
energies, i.e., where \( E = Ck^2 \to 0 \). Since \( \tan \varphi_3 \approx -(kr_0)^{-1} \) (\( r_0 \) is the scattering length),
and, according to Levinson theorem [60], the phase shift \( \delta(k) \approx n\pi \) (\( n = 7 \) for the PEC
in question) as \( k \to 0 \), one comes to the following expression for the wave function in this
region: \( \Psi(r) \approx 2k(r - r_0) \). This is explicitly demonstrated by a dotted line in the top graph
of Fig. 6, where the vertical dotted line indicates the position of the characteristic parameter
\( r_0 \). Naturally, such a simple linear coordinate dependence appears only at distances where
the potential well becomes insignificant, i.e., \( V(r) \approx 0 \), but, on the other hand, \( r \ll \frac{\varphi}{2k} \).

The scattering wave functions for the ground state reference PEC, along with the full set
of bound state wave functions (only 7 in total), have been used as the basis to accurately
ascertain all details of the Franck-Condon factors. Throughout the whole domain, the wave
functions have been calculated at the abscissas of the 5-point Gaussian quadrature formula
related to the intervals of 0.02 Å width. Some results of these calculations are shown in
Figs. 4, 5, and 7 to 9. In Fig. 7 one can see the Franck-Condon factors for bound-free
transitions from the selected vibrational levels of both \( 0^+_u \) and \( 1_u \) reference PECs, while the
details of the Franck-Condon spectrum from the highest level (\( v' = 29 \)) of the \( 0^+_u \) state are
demonstrated in Fig. 8. Note that the actual calculated probability density distributions
are shown on both figures. From these data one can easily ascertain the probability of spontaneous emission \( (p_{v'}) \) as well as the radiative lifetime \( (\tau_{v'} = 1/p_{v'}) \) of the levels. As
explained in handbooks on quantum mechanics (see, e.g., [58]),

\[
p_{v'} = \frac{4}{3\hbar^4c^3} \sum_{v''} (E_{v''} - E_{v'})^3 \left[ \int_0^\infty \Psi_{v''}(r)\mu(r)\Phi_{v'}(r)dr \right]^2 \\
+ \int_0^{\infty} (E_{v'} - E)^3 \left[ \int_0^\infty \Psi(E, r)\mu(r)\Phi_{v'}(r)dr \right]^2 dE,
\]

where \( E_{v'} \) and \( \Phi_{v'}(r) \) denote the initial (fixed) energy level and its wave function, while \( E_{v''} \).
and $E$ are the discrete and continuous energy eigenvalues, respectively, with corresponding eigenfunctions $\Psi_{v'}(r)$ and $\Psi(E, r)$. The calculations can be conveniently carried out using atomic units, i.e., taking $\hbar = 1$, the velocity of light $c = 137.03604$, and measuring energy in Hartrees (1 Hartree = 27.2116 eV). Conversion to the SI frequency unit (Hz) is elementary: $1 \text{ Hz} = 24.188843 \times 10^{-18}$ a.u.

What are actually depicted in Figs. 7 and 8 are the energy integrands of the second term of Eq. (14) for the selected levels (including the factors $\frac{4}{3\hbar^2c}$ and $(E_{v'} - E)^3$). The low-energy part of the calculated spectra for the $0_{u}^+$ state (see the top graphs in Figs. 7 and 8) nicely agrees with the experimental results by Möller et al. [24], which confirms their assignment to the inner turning point region of the excimer’s high-lying levels. On the other hand, this is an evidence of the validity of the \textit{ab initio} PECs by Fernández and Koch [47]. As demonstrated in Fig. 7, the maximum of the second continuum is expected near 9.8 eV, which is also in full agreement with experimental observations.

Another interesting result can be seen in the bottom graph of Fig. 8, which is related to the region where $E \to 0$, and, consequently, a very small energy step (0.001 meV) has been used. Namely, since $\Psi(E, r) \to 0$ as $E \to 0$, the high-energy part of the probability density distribution looks like cut off. Indeed, the squared wave function of the $v' = 29$ level, as needed, has 30 maxima, while only 28 maxima are seen for the related Franck-Condon spectrum in Fig. 8. Naturally, this simply means that one has to take the bound-bound transitions also into consideration. These contributions for the selected vibrational levels of both $0_{u}^+$ and $1_{u}$ excimer states are shown in Fig. 9. The discrete sets of 7 points ($v'' = 0 \div 6$) there may seem to be located somewhat irregularly, but in fact, their positions are by no means accidental. On the contrary, as demonstrated in Figs. 4 and 5, the total integrated transition probability curves according to Eq. (14) are nice and smooth, although their bound-bound and bound-free constituents as if show some roughness. Such a behavior of the total probability is, of course, not only expected but even required. Indeed, this is nothing else but an indication of the completeness of the basis and the correctness of normalization of the wave functions. The overall transition probability for all levels should be exactly the same, if one puts $\mu(r) = 1$ and ignores all factors in Eq. (14). Smoothly changing total probabilities simply reflect the smooth coordinate dependencies of the transition moment.
For any diatomic system, one can construct an exactly solvable multi-component reference potential based on the available experimental data. In this paper, we described a possible strategy to achieve this goal, which is analytically simple and computationally straightforward. It is based on composing the reference PECs of several smoothly joined Morse-type potentials, and this was not an accidental choice. One might think that there are lots of alternatives, but this is not quite the case. Indeed, for any shape invariant potential one can easily find the exact solution of the related Schrödinger equation [44]. The point is, however, that they are already the physically correct linear combinations of special solutions, which can be easily ascertained only because the specific analytic form of the potential remains the same in the whole physical domain. The situation changes dramatically, if the potential consists of several analytically different pieces. Then it is often possible to easily ascertain one special solution but rarely both of them. A well-known exception is the piece-wise linear potential possessing two linearly independent solutions in terms of Airy functions [61], nowadays available as standard functions in math-oriented programming languages. A useful method of solving the Schrödinger equation for a piece-wise linear reference PEC has been worked out long ago by Gordon [62].

Another well-known example for which the two linearly independent solutions can be given in a simple analytic form is the Morse-type PEC analyzed in this paper. The classical Morse potential [43] itself is a reasonable approximation, but by introducing several components one can get a much more realistic description. Differently from a piece-wise linear potential, the components can be smoothly joined, preserving the continuity of the PEC and its derivative. The two linearly independent solutions of the related Schrödinger equations can be always given in terms of the well-studied confluent hypergeometric functions, and their correct linear combinations are determined by the boundary conditions and continuity requirements.

The result of the fitting procedure depends not only on the theoretical methods and computational techniques applied, but also on the reliability of the experimental data and the constraints adopted. For example, following Fernández and Koch [47], we fixed the equilibrium nuclear separation $R_e = 2.3893$ Å for both $0_u^+$ and $1_u$ excimer states, but we cannot claim this to be the conclusive value for $R_e$ (slightly different results have been
reported by other authors). Since the transitions from the bottom of the excimer states fall into the repulsive wall of the ground state, the position of the second emission continuum strongly depends on $R_e$. It means that if one assumes a different value for this parameter, the ground state PEC has to be changed as well. Another issue which probably needs further confirmation is the absolute numbering of the observed vibrational levels $^{30}$, because the resulting PECs are rather sensitive to their changing.

Nevertheless, as we demonstrated, a good fit with the experimental data has been achieved, and this is a strong argument for the reliability of the PECs obtained in this paper. The potentials involve a wide range of nuclear separations ($r \gtrsim 1.9$ Å) and they can be used to study the most important spectroscopic features of Ar$_2^*$ excimers, including the details of their emission continua. In addition, they are expected to be useful for the analysis of the relaxation dynamics and the time-resolved emission spectra of the excimers. However, let us recall once again that these approximate PECs and the relevant transition moments have been deduced on the relatively modest basis of the available experimental data, following the relatively "soft" criteria stated in Section II. Hopefully, the results of this work can stimulate further experimental research to reveal much more details about the properties of the RG excimers.

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Figure captions

Fig. 1. Four-component reference potential (solid line) for the ground electronic state of Ar\textsubscript{2} in comparison with two \textit{ab initio} potentials. The open circles in both graphs (and in the inset) correspond to \cite{47}, while the dotted curve in the upper graph is taken from \cite{48}. The same reference PEC (solid line) is depicted in both graphs, but essentially different energy scales are used for them. All components have the well-known analytic form of the Morse potential, but the ordinary Morse approximation is used only in the central range $r \in [X_2, X_3]$ (see the lower graph). Two pseudo-Morse components for the regions $r \leq X_1$ and $r \in [X_1, X_2]$, respectively, have been introduced, while the long-distance range $r \geq X_3$ is approximated by a reversed Morse potential. The inset demonstrates that the RM approximation (dotted curve) does not contradict to the inverse power series expansion $-C_6/r^6 - C_8/r^8 - C_{10}/r^{10}$ (dashed curve). The parameters $C_6, C_8, \text{and} C_{10}$ are taken from \cite{17}, while the RM parameters for this specific fit are as follows: $R_{\text{max}} = 12.45$ Å, $V_0 = -0.1268$ meV, $D = -1.799\text{E}-4$ meV, and $\alpha = 0.66$ Å\textsuperscript{-1} ($V(R) = V_0 + D \times [\exp(-\alpha \times (R - R_m)) - 1]^2$).

Fig. 2. Reference potentials for the three electronic states of Ar\textsubscript{2} examined in this paper. The parameters of the ground-state potential in the lower graph (the same as in Fig. 1) have been determined from the least squares fit to the \textit{ab initio} potential by Fernández and Koch \cite{47}, while the curves for the excimer states 0\textsuperscript{+}\textit{u} and 1\textit{u} have been constructed with the help of the fitting procedure described in Sections II B and C, respectively. The corresponding 1\textit{u} $\rightarrow$ 0\textsuperscript{+}\textit{g} and 0\textsuperscript{+}\textit{u} $\rightarrow$ 0\textsuperscript{+}\textit{g} transition moments are also shown in the upper graph (note that different scales are used for them), where the dotted line has been taken from \cite{47}.

Fig. 3. A more detailed depiction of the three-component reference potential for the 0\textsuperscript{+}\textit{u} state (upper graph), and the calculated vibrational energies for both excimer states in comparison with the observed data (lower graph). As in the experiments, the position of the levels is measured relative to the zeroth level of the ground state. The $v' = 31$ level of the 1\textit{u} state was taken from \cite{57}, all other experimental data are those from \cite{30}.

Fig. 4. Upper graph: calculated probabilities of bound-free and bound-bound transitions
starting from the vibrational levels of the $0_u^+$ state. Lower graph: corresponding radiative lifetimes of all levels. The lifetime of the zeroth level ($\tau_0 = 4.19$ ns) practically coincides with the experimental result ($\tau_0 = 4.20 \pm 0.13$ ns) from [56].

Fig. 5. The same as in Fig. 4 but for the $1_u$ excimer state. Again, the lifetime of the zeroth level ($\tau_0 = 3.15$ µs) is close to the experimental one ($\tau_0 = 3.2 \pm 0.3$ µs) from [56]. Good agreement between the theoretical and experimental lifetimes for the levels $v' = 24 \div 30$ is also demonstrated (see Table 3).

Fig. 6. A selection of the scattering ($E > 0$) wave functions for the ground state (for correct energy normalization they have to be multiplied by $F = \left(4\pi\sqrt{EC}\right)^{-1/2}$, where $C = \frac{\hbar^2}{2m}$). The upper graph corresponds exactly to the top of the tiny artificial potential barrier (see the explanations in Section II B and Table 1), i.e., $E = 1.029793 \times 10^{-7}$ eV. Due to the extremely small $E = Ck^2$, one can see nearly linear coordinate dependence, $\Psi(r) \approx 2k(r - r_0)$ ($r_0$ is the scattering length), in the range where $V(r) \approx 0$ but $r \ll \frac{\pi}{2k}$. The three lower graphs correspond to $E = 1$ meV, $E = 100$ meV, and $E = 4$ eV, respectively, when the wave function more or less rapidly achieves its asymptotic free-wave form.

Fig. 7. Demonstration of the calculated Franck-Condon factors for the bound-free transitions from the selected vibrational levels of the excimer states. One can infer that the first and the second emission continua (with maximum near 9.8 eV) are formed just where expected, while the low-energy part of the spectrum nicely agrees with the experimental results by Möller et al. [24] under selective synchrotron radiation excitation.

Fig. 8. Demonstration of the details of the Franck-Condon spectrum for the bound-free transitions from the highest level of the $0_u^+$ state (shown also in Fig. 7). The lower graphs begin exactly at the energies where the upper graphs end. The bottom graph (where open circles mark the actually calculated intensities) is cut off at $E = 0$, and therefore the overall spectrum shows only 27 zeros (instead 29). The ”missing” part corresponds to bound-bound transitions.

Fig. 9. Depiction of the Franck-Condon factors for bound-bound transitions from the selected vibrational levels of the $0_u^+$ (upper graph) and $1_u$ (lower graph) excimer states of Ar$_2$. The related atomic levels $^3P_1$ and $^3P_2$ are shown by the arrows. Location of the points
corresponding to the highest levels may seem irregular, but in fact, their positions are
determined by rigorous quantum mechanical sum rules (see also Figs. 4 and 5).
TABLE I: Parameters of the reference potential for the ground electronic state of Ar$_2$. The positions of the vibrational levels (in meV, relative to the bottom of the potential well) are also given.

| $k$ | Type | $V_k$ (meV) | $D_k$ (meV) | $\alpha_k$ (1/Å) | $R_k$ (Å) | Range (Å) |
|-----|------|-------------|-------------|-------------------|-----------|-----------|
| 0   | PM   | -67.83414   | 0.0763369   | 1.708238         | 5.224252  | $r \leq 2.9105$ |
| 1   | PM   | -15.42556   | 0.137657    | 2.293931         | 4.443077  | $r \in [2.9105, 3.35]$ |
| 2   | OM   | -12.0866    | 11.85914    | 1.729656         | 3.7769    | $r \in [3.35, 4.4891]$ |
| 3   | RM   | 1.029793E-4 | -1.029793E-4| 0.6877276        | 12.4891   | $r \geq 4.4891$ |

| $v''$ | 0   | 1   | 2   | 3   | 4   | 5   | 6   |
|-------|-----|-----|-----|-----|-----|-----|-----|
| This work | 1.8485 | 5.0741 | 7.6651 | 9.6403 | 10.9256 | 11.7307 | 12.0699 |
| Ref. 46 | 1.8127 | 4.9470 | 7.4416 | 9.3224 | 10.6342 | 11.4488 | 11.8691 |
| Ref. 30 | 1.8263 | 5.0102 | 7.5619 | 9.4923 | 10.8462 | 11.6918 | -   |
TABLE II: Parameters of the reference potential for the $0^+_u$ state of Ar$_2$. The vibrational energies given in meV are measured relative to the bottom of the potential well (this work), while the values in cm$^{-1}$ are transition energies relative to the zeroth level of the ground state, as in [30]. The calculated spectroscopic constants are as follows: $\omega_e = 296.26$ cm$^{-1}$, $D_e = 6128.3$ cm$^{-1}$.

| $k$ | Type | $V_k$ (meV) | $D_k$ (meV) | $\alpha_k$ (1/Å) | $R_k$ (Å) | Range (Å) |
|-----|------|-------------|-------------|----------------|-----------|----------|
| 1   | OM   | 10864.76    | 1166.681    | 1.66221         | 2.3893    | $r \leq 3.0407$ |
| 2   | RM   | 11624.65    | -0.6649193  | 1.654645        | 4.862433  | $r \in [3.0407, 4.16]$ |
| 3   | RM   | 11623.59    | -3.021853E-9| 3.588833        | 7.00      | $r \geq 4.16$   |

| $v'$ | 0  | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|------|----|----|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 18.2936 | 54.4470 | 90.0222 | 125.0192 | 159.4380 | 193.2786 | 226.5409 | 259.2250 |

| $v'$ | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 |
|------|----|----|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 291.3308 | 322.8584 | 353.8078 | 384.1790 | 413.9720 | 443.1867 | 471.7515 | 499.7937 |

| $v'$ | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|------|----|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 527.2506 | 553.8589 | 579.4339 | 603.7447 | 626.7231 | 648.2718 | 668.2571 |
| $E_{v'}$ (cm$^{-1}$) | 92766.9 | 92940.7 | 93101.9 |
| Exp., Ref. 30 (cm$^{-1}$) | 92769.3 | 92935.9 | 93093.5 |

| $v'$ | 23 | 24 | 25 | 26 | 27 | 28 | 29 |
|------|----|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 686.6108 | 703.2166 | 717.9872 | 730.8195 | 741.5951 | 750.1805 | 756.3843 |
| $E_{v'}$ (cm$^{-1}$) | 93249.9 | 93383.9 | 93503.0 | 93606.5 | 93693.4 | 93762.6 | 93812.7 |
| Exp., Ref. 30 (cm$^{-1}$) | 93241.2 | 93377.6 | 93501.6 | 93610.8 | 93701.3 | - | - |
TABLE III: Parameters of the reference potential for the $1_u$ state of Ar$_2$. The vibrational energies given in meV are measured relative to the bottom of the potential well, while the values given in cm$^{-1}$ are the transition energies relative to the zeroth level of the ground state. The corresponding experimental values are from [30], except $E_{31}$, which was taken from [57]. The following spectroscopic constants were obtained for the $1_u$ state: $\omega_e = 287.30$ cm$^{-1}$ and $D_e = 5929.6$ cm$^{-1}$.

| $k$ | Type | $V_k$ (meV) | $D_k$ (meV) | $\alpha_k$ (1/Å) | $R_k$ (Å) | Range (Å) |
|-----|------|-------------|-------------|------------------|-----------|-----------|
| 1   | OM   | 10813.17    | 850.0       | 1.888481         | 2.3893    | $r \leq 3.39001$ |
| 2   | RM   | 11548.17    | -0.005519566 | 1.654645         | 6.390011  | $r \in [3.39001, 5.5]$ |
| 3   | RM   | 11548.35    | -1.515516E-10 | 0.730545        | 20.0      | $r \geq 5.5$ |

| $v'$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|------|---|---|---|---|---|---|---|
| $E_{v'}$ (meV) | 17.7170 | 52.5912 | 86.7190 | 120.1005 | 152.7356 | 184.6243 | 215.7667 |

| $v'$ | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|------|---|---|---|---|---|----|---|
| $E_{v'}$ (meV) | 246.1627 | 275.8123 | 304.7156 | 332.8725 | 360.2830 | 386.9472 | 412.8650 |

| $v'$ | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|------|----|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 438.0364 | 462.4614 | 486.1401 | 509.0725 | 531.2584 | 552.6980 | 573.3912 |

| $v'$ | 21 | 22 | 23 | 24 | 25 | 26 | 27 |
|------|----|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 593.3381 | 612.4904 | 630.8586 | 648.2035 | 664.3098 | 679.0578 | 692.3569 |
| $E_{v'}$ (cm$^{-1}$) | 92384.2 | 92524.1 | 92654.0 | 92772.9 | 92880.2 |

Exp., Ref. 30 (cm$^{-1}$) | 92386.7 | 92524.5 | 92653.1 | 92771.4 | 92879.1 |
Rad. lifetime (ns) | 182.1 | 169.0 | 159.3 | 152.9 |
Exp., Ref. 31 (ns) | 173 ± 17 | 162 ± 14 | 167.2 ± 9.0 | 161.7 ± 9.4 |

| $v'$ | 28 | 29 | 30 | 31 | 32 | 33 |
|------|----|----|----|----|----|----|
| $E_{v'}$ (meV) | 704.0696 | 714.0975 | 722.3222 | 728.6210 | 732.8645 | 734.8840 |
| $E_{v'}$ (cm$^{-1}$) | 92974.7 | 93055.5 | 93121.9 | 93172.7 | 93206.9 | 93223.2 |

Experiment (cm$^{-1}$) | 92974.8 | 93056.9 | 93123.7 | 93171.0 | - | - |
Rad. lifetime (ns) | 149.6 | 149.4 | 152.1 | 158.0 | 167.5 | 185.6 |
Exp., Ref. 31 (ns) | 157.4 ± 9.6 | 155.7 ± 9.0 | 166 ± 11 |