Long Range Potentials for Two Na$(3p)$ Atoms Including Ionic-Covalent Interaction and Fine Structure: Application to Two-Color Photoassociation Spectroscopy

O. Dulieu,[1] B. Lévy,[2] S. Magnier,[3] F. Masnou-Seeuws,[1] and Ph. Millié[4]
[1] *Laboratoire Aimé Cotton, Bâtiment 505, Université Paris-Sud, 91405 Orsay Cedex, France*
[2] *Groupe de Chimie Quantique, Bâtiment 337, Université Paris-Sud, 91405 Orsay Cedex, France*
[3] *LASIM, Bâtiment 205, Université Claude Bernard Lyon I, 69622 Villeurbanne Cedex, France*
[4] *SPAM, Centre d'Etudes Nucléaires de Saclay, 91191 Gif sur Yvette, France*

(Received 28 November 1995)

In the framework of *ab initio* pseudopotential calculations, a method is presented to compute an effective spin-orbit Hamiltonian within a nonorthogonal diabatic representation separating the ionic and covalent subspaces. The resulting Hund's case *c* adiabatic curves display long range structures. We predict that a small (≈ 1 cm^{-1}) fine-structure splitting of an ionic $^3\Pi_u$ curve is manifested in the spectrum of the excited Na$_2$ molecule slightly below the $(3p\,^2P_{1/2} + 3p\,^2P_{1/2})$ asymptote as a series of well identified quadruplets. They should be observed in two-color photoassociation spectroscopy experiments using cold atoms.

PACS numbers: 31.15.Ar, 32.80.Pj, 34.50.Rk

The fundamental problem of the accurate description of long range interaction between two atoms (van der Waals forces), which has been extensively studied in the past [1,2], is presently reopened due to rapid progress in laser cooling and trapping of atoms [3,4]. Photoassociative spectroscopy (PAS) in a cold atom medium [5], as well as elaborate developments in traditional laser spectroscopy [6], are now capable of providing data on weakly bound states of diatomic molecules, for which the vibrational motion extends towards interatomic distances of several hundreds of atomic units (1 a.u. $= a_0 = 5.29177 \times 10^{-9}$ m) that is much larger than in all previous investigations. Up to now, most experimental results are related to the electronic states of Li$_2$ [7], Na$_2$ [6,8], and Rb$_2$ [9] dimers that are correlated to the $ns + np$ dissociation limit, where one atom is in the ground state and the other one in the first excited state. The long range potentials deduced from such measurements are in good agreement with theoretical calculations [10,11] using asymptotic methods. However, more recent two-color PAS experiments investigate upper excited electronic states, correlated to the Na$(3p)$ + Na$(3p)$ asymptote [12,13]; they detect the ion signal produced from short range autoionizing doubly excited states correlated to a given long range state. The interpretation of such spectra is a challenge because the pattern of electronic states is much more complicated than for the $3s + 3p$ asymptote. Although the short range autoionizing states are now well identified [14], the correct evaluation of intermediate and long range potentials, typically in the $20a_0$–$50a_0$ range of internuclear distances, is still an open problem. Indeed, as the $(3p + 3p)$ asymptote cannot be considered as an isolated energy level, second order perturbation theory is no longer a valid approximation to compute the dispersion forces. The asymptotic estimation of tunneling exchange forces cannot follow the usual treatment [15,16], since the covalent states are perturbed by several ionic states [17], some of which correspond to excited states of the negative ion. Finally, the correct treatment of spin-orbit coupling [18] appears difficult in this context of strong configuration mixing.

However, recent results seem to indicate that quantum chemistry calculations using effective potentials can provide an alternative approach: Good accuracy has been obtained for the ground and a large number of excited states of Na$_2$ [19], NaK, and K$_2$ [20] up to distances as large as $50a_0$. The aim of the present paper is to extend such results to the determination of potential curves in Hund's case *c* coupling scheme for the long range states of Na$_2$ correlated to Na$(3p)$ + Na$(3p)$.

Our procedure consists in four steps of molecular calculations at large distances: (1) adiabatic states neglecting fine-structure splitting (Hund's case *a*) → (2) diabatic states separating ionic and covalent subspaces and neglecting fine structure → (3) diabatic covalent states including fine-structure splitting in the framework of Hund's case *c* coupling scheme → (4) adiabatic states in Hund's case *c* coupling scheme, which are then correlated to short range autoionizing diabatic states.

Step 1 has been realized by Magnier *et al.* [19] for internuclear distances up to $50a_0$: Their *ab initio* pseudopotential calculations introduce effective potentials to represent core-polarization effects [21]. Long range pseudocrossings are manifested for various symmetries [17,19,20] due to the interaction between covalent states, dissociating into Na(nl) + Na$(n'l')$, and ionic states, dissociating into Na$^+$ + Na$^-$. In the latter case the negative ion is either in the ground state ($^1\Sigma^+_{g,u}$ symmetries) or in an excited autoionizing state ($^3\Pi_{g,u}$ symmetries) stabilized by the Coulomb attraction of the Na$^+$ ion. An example of such pseudocrossings is manifested in Fig. 1(a), where the $^3\Pi_u$ covalent states are perturbed in the vicinity of $R = 26a_0$ by an ionic excited state correlated to Na$^+$ + Na$^{-*}(3s3p,\,^3P^o)$.

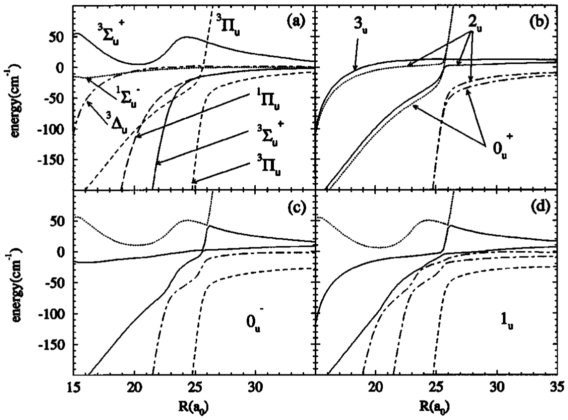

FIG. 1. Adiabatic Na_2 long range potential curves for the ungerade $(3p + 3p)$ manifold, in the vicinity of the $^3\Pi_u$ avoided crossing ($R \approx 26a_0$). The origin of energies is taken at the $(3p + 3p)$ dissociation limit. (a) Hund's case a adiabatic potential curves. (b)–(d) Hund's case c adiabatic potential curves dissociating into $P_{1/2} + P_{1/2}$ at $-22.928\ \text{cm}^{-1}$ (dashed line), into $P_{3/2} + P_{1/2}$ at $-5.732\ \text{cm}^{-1}$ (dot-dashed line), into $P_{3/2} + P_{3/2}$ at $+11.464\ \text{cm}^{-1}$ (solid line), and into $3s + 4d$ at $588.6\ \text{cm}^{-1}$ (dotted line).

In step 2, we project out the ionic and covalent states using a diabatization procedure in a set of nonorthogonal states [22,23]. Within the full configuration space described in [19], we first define the subspace $\mathcal{E}_1$ of the N lowest eigenstates $|\Phi_i\rangle$ (with *adiabatic* energy E_i) of the electronic Hamiltonian $\mathbf{H}$, which, in $\mathcal{E}_1$, is represented by the effective operator $\mathbf{H}_1 = \sum_{i=1}^{N} |\Phi_i\rangle E_i \langle\Phi_i|$. Then we define a subspace $\mathcal{E}_2$ of N *nonorthogonal* wave functions $|\overline{\Psi}_l\rangle$ of the same total symmetry consisting of (i) $N - n_i$ antisymmetrized products of atomic functions on both centers describing the first $N - n_i$ dissociation limits $\text{Na}(nl) + \text{Na}(n'l')$ of the adiabatic states; (ii) n_i wave functions for the ground and excited states of the negative ion, obtained by a full configuration interaction in a subspace of antisymmetrized products of atomic orbitals on one center. The projection of the adiabatic wave functions on the subspace $\mathcal{E}_2$ is

$$|P\Phi_i\rangle = \sum_{l,m=1}^{N} |\overline{\Psi}_l\rangle \overline{S}_{lm}^{-1} \langle\overline{\Psi}_m|\Phi_i\rangle, \tag{1}$$

with $\overline{S}_{lm} = \langle\overline{\Psi}_l|\overline{\Psi}_m\rangle$. Orthonormalized projections $|\overline{\Phi}_i\rangle$ are obtained by a standard procedure [24]:

$$|\overline{\Phi}_i\rangle = \sum_{j=1}^{N} |P\Phi_j\rangle (S_{ji})^{-1/2}, \tag{2}$$

where $S_{ji} = \langle P\Phi_j|P\Phi_i\rangle \equiv \langle\Phi_j|P\Phi_j\rangle$. We then define an effective Hamiltonian $\mathbf{H}'$ in $\mathcal{E}_2$ by its matrix elements:

$$\begin{aligned} H'_{lm}(R) &= \langle\overline{\Psi}_l|\mathbf{H}'|\overline{\Psi}_m\rangle \\ &= \left\langle \overline{\Psi}_l \,\middle|\, \sum_{i=1}^{N} \,\middle|\, \overline{\Phi}_i \right\rangle E_i(R) \langle\overline{\Phi}_i|\overline{\Psi}_m\rangle . \end{aligned} \tag{3}$$

In (3), the diagonal matrix elements are interpreted as diabatic energies, while the nondiagonal elements are the electronic coupling terms. By constructure, the eigenvalues obtained by diagonalization of $\overline{\mathbf{S}}^{-1/2}\mathbf{H}'\overline{\mathbf{S}}^{-1/2}$ in $\mathcal{E}_2$ are identical to the set of N adiabatic energies $E_i(R)$. It is expected that in contrast with these energies, the matrix elements $H'_{lm}(R)$ are smoothly varying functions of R, well adapted to an interpolation procedure. The size of the subspace $\mathcal{E}_2$ is optimized by checking that for each adiabatic state $|\Phi_i\rangle$ the condition $\sum_{m=1}^{N}\langle\Phi_i|\overline{\Psi}_m\rangle = 1$ is verified with an accuracy better than 10^{-3}. For $R > 14a_0$, and in the range of energies considered here, the convergence of the diabatization procedure was obtained by including all the covalent states associated to dissociation limits from $\text{Na}(3s) + \text{Na}(3s)$ up to $\text{Na}(3s) + \text{Na}(4f)$, and only two ionic states dissociating into $\text{Na}^+ + \text{Na}^-(^1S)$ and $\text{Na}^+ + \text{Na}^-(^3P^o)$. At internuclear distances $R < 14a_0$, a larger number of ionic and covalent states should be included, but this is beyond the scope of the present paper.

In step 3, we introduce the fine-structure interaction as an effective Hamiltonian $\mathbf{H}_{\text{fs}}$ [25] with nonzero matrix elements only for the $3s + 3p$ and $3p + 3p$ covalent configurations. In view of *ab initio* estimations [26], we have assumed that at large internuclear distances the fine-structure splitting is the same as that for an isolated atom, $\Delta E_{\text{fs}} = 17.196\ \text{cm}^{-1}$. Neglect of fine-structure splitting for Rydberg states is justified in the framework of the accuracy of the present molecular calculations. Neglect of fine-structure splitting for the ionic states seems reasonable from the present knowledge of negative ions [27], but should be discussed. However, due to the rapid $1/R$ variation of the ionic curves, the location of the crossing point between ionic and covalent curves is not modified when a small shift in the ionic energy is considered. Therefore the main conclusions of the present paper would not change if a fine-structure splitting was introduced for the negative ion. Whereas $\mathbf{H}'$ is block diagonal for the various symmetries $^{2S+1}\Lambda_{u,g}$, the total effective Hamiltonian $\mathbf{H}_{\text{tot}} = \mathbf{H}' + \mathbf{H}_{\text{fs}}$ in $\mathcal{E}_2$ contains coupling terms between the covalent states with different values of the quantum number $\Lambda = 0, 1, 2$ and $S = 0, 1$.

In step 4, we have diagonalized $\overline{\mathbf{S}}^{-1/2}\mathbf{H}_{\text{tot}}\overline{\mathbf{S}}^{-1/2}$ in $\mathcal{E}_2$ [24] in order to obtain the long range adiabatic energies for the values 0,1,2,3 of the quantum number Ω. The results differ markedly from asymptotic calculations by Kowalczyk [28], and Heather and Julienne [29] as well as from earlier *ab initio* calculations [30]: The differences can be interpreted as mainly due to the contribution of ionic states. Typically, the discrepancies between our curves and purely covalent ones are $\approx 1\ \text{cm}^{-1}$ at $40a_0$ and up to $10\ \text{cm}^{-1}$ at $30a_0$. The potential curves of u symmetry, correlated to the three dissociation limits $\text{Na}(3p\ ^2P_J) + \text{Na}(3p\ ^2P_{J'})$, with $(J, J') = (\frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, \frac{3}{2}), (\frac{3}{2}, \frac{3}{2})$, are represented in Figs. 1(b)–1(d), to be compared with the Hund's case a curves of Fig. 1(a). The potential barrier that appears in the $^3\Sigma_u^+$ curve in Fig. 1(a) survives for the 0_u^- and 1_u symmetries. Because of fine-structure mixing, the pseudocrossing between the two $^3\Pi_u$ curves in Fig. 1(a) is now present for all symmetries Ω_u provided $\Omega \leq 2$. The lowest curves in Figs. 1(b)–1(d) look very similar to the lowest $^3\Pi_u$ curve for internuclear distances smaller than the position $R_0 \approx 26a_0$ of the pseudocrossing, where a strong ionic character is manifested. However, when the spin-orbit coupling is taken into account, a splitting is introduced between the various components, due to a different admixture of covalent states with the ionic state. This is illustrated in the inset of Fig. 2, where we show, in the vicinity of the pseudocrossing region, a detailed view of the lowest "Hund's case c" 0_u^- and 1_u curves, which are adiabatically correlated to the $(\frac{1}{2}, \frac{1}{2})$ asymptote and of the lowest 0_u^+ and 2_u curves correlated to the $(\frac{3}{2}, \frac{1}{2})$ asymptote. The small splitting ($\approx$1 cm^{-1}) between these curves leads us to predict that well identified multiplet structures should be observed in the spectrum of the excited Na_2 molecule in an energy region slightly below the $(\frac{1}{2}, \frac{1}{2})$ asymptote. As the long range $^3\Pi_u$ state has been shown to be correlated to a short range autoionizing doubly excited state [14], we suggest that two-photon PAS should be an efficient way of checking such structures by detection of ion or electron signal.

We therefore have represented in Fig. 2 an excitation scheme for experimental conditions similar to the NIST experiment [12]. In the first step, we consider a free-bound transition with absorption of a photon, slightly red detuned compared to the frequency ω_0 of the D_2 line, by a pair of two colliding cold atoms. In the following, we have chosen the detuning δ so that the rovibrational level ($v_i = 48, J_i = 1$) of the long range 1_g state is populated. A second photon with frequency $\omega_0 - (\delta + \delta')$ next populates a vibrational level v_f in one of the four long range Ω_u curves described above, all correlated to the short range autoionizing doubly excited $^3\Pi_u$ diabatic state. In contrast with δ, the additional detuning δ' can be positive or negative. The horizontal line in the inset of Fig. 2 holds for $\delta' = 0$. When δ' is varied the detection of an ion is the signature of the presence of a bound $\Omega_u(v_f, J_f = 0, 1, 2)$ level. We have chosen δ' so that in this second step the vibrational wave function v_f has an outer turning point located left of the crossing point $R < R_0 \approx 26a_0$. Also indicated in Fig. 2 is the possibility of populating an upper long range curve, correlated at short distances to an autoionizing $^1\Pi_u$ doubly excited curve, with even smaller distance for the outer turning point. This second state is expected to have a much smaller contribution due to the unfavorable overlap with the v_i vibrational wave function. The absorption probability in the second step is proportional to the square matrix element of the molecular transition dipole moment between the two levels, which for simplicity's sake is assumed proportional to a Franck-Condon factor. Because of the small values of the computed rotational constants (in the range 0.015 to 0.018 cm^{-1} for all the levels involved in the present scheme), the Franck-Condon factors are identical for P, Q, and R branches so that we shall discuss only the Q branch. The resulting model spectrum is represented in Fig. 3, demonstrating the well resolved multiplet structure mentioned above. We have represented details of the multiplet in the case $v_f = 137$. The first two lines, separated by less than 0.1 cm^{-1}, correspond to the 0_u^- and 0_u^+ long range states, then the 1_u line is located at 0.2 cm^{-1} further, while the 2_u line is separated by a larger splitting $\approx$1 cm^{-1}. The intensities of the four lines are approximately equivalent, and their Franck-Condon variation is displayed in the inset of Fig. 3: Marked differences appear between the various components when the outer turning point of the final vibrational wave function comes close to the pseudocrossing at $R \approx 26a_0$ ($v_f = 142$). For a turning point located beyond $26a_0$, we expect very different multiplet structures corresponding to splittings of the order of the atomic fine structure ($\approx$17 cm^{-1}). We have explored various values of vibrational numbers v_i, leading to somewhat different intensity patterns; however, the four-component multiplet is always observable, except when the region of the pseudocrossing at $R \approx 26a_0$ is experienced, inducing strong perturbations in the spectra. Because of the very limited number of J values in the experimental spectra, these structures should be readily observable.

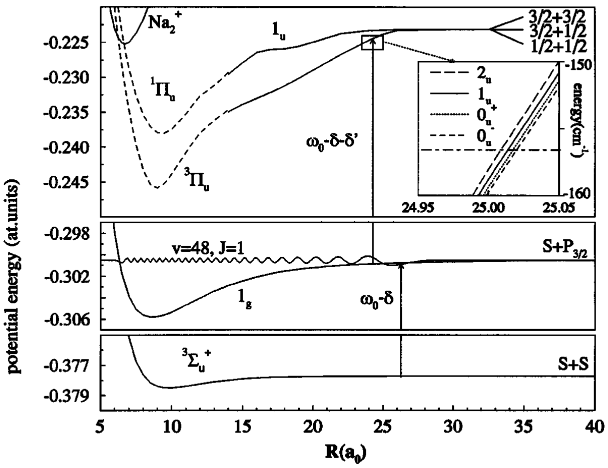

FIG. 2. Two-color photoassociation scheme in conditions similar to Ref. [12]. The first photon is red detuned by δ (84 cm^{-1} in the present model) from the D_2 line at frequency ω_0. The wave function of the populated vibrational level is represented. The frequency of the second photon is shifted by $-\delta'$ from the first one, exciting vibrational levels of doubly excited states with outer turning point located at internuclear distance $R < 26a_0$. The ground state of the final molecular ion is also represented. For clarity, only two long range Hund's case adiabatic potential curves are displayed (full lines), correlated to short range autoionizing curves (dashed lines). The lower curve splits, in fact, into four curves, as shown in the inset. The horizontal line corresponds to the energy reached via a one-color, two-photon excitation from the $(3s + 3s)$ limit $(\delta' = 0)$.

In conclusion, the present paper has shown how the difficult problem of calculating the long range curves of the alkali dimers correlated to the first doubly excited asymptote could be solved by very simple calculations. The

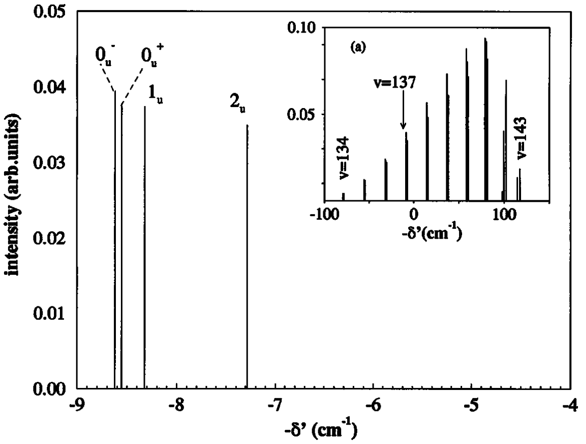

FIG. 3. Predicted ion spectra for a PAS experiment similar to Ref. [12], as a function of the additional shift ($-\delta'$) of the frequency $\omega = \omega_0 - \delta - \delta'$ of the second photon. The inset (a) shows the spectra for a larger range of δ' (in cm^{-1}).

ionic-covalent pseudocrossings, often neglected in theoretical treatments, have been shown to play a key role in the shape of the potential curves. We have shown that many structures are present in the excited curves, which should manifest themselves in the observed spectrum. The present paper has been focused on the lowest curves of u symmetry, which have a strong ionic character for $R < 26a_0$ and, due to a weak covalent component, display a very small ($\approx$1 cm^{-1}) fine-structure splitting. They enable us to predict well resolved multiplet structures in the spectrum, which can be checked by two-color photoassociation spectroscopy. As the accuracy of the calculations is not the experimental one, we cannot predict the absolute position of the lines, but a very characteristic qualitative pattern of four lines, two of which are distant by less than 0.1 cm^{-1}. As such patterns are strikingly similar to some observed structures [12], the present theoretical method seems promising for interpretation of two-color photoassociation spectra. It would be interesting to verify that they disappear when the frequency of the two lasers is varied so that the vibrational state populated in the second step has an outer turning point larger than $26a_0$. Other structures could also be analyzed in the upper curves of u symmetry, for instance, the barrier and long range well in the $8^3\Sigma_u^+$ curve. Similar effects are present in the curves of g symmetry and will be discussed in a forthcoming paper.

The authors are very grateful to P. D. Lett for making his results available before publication, and for many stimulating discussions. This work has been performed in the framework of the Human Capital and Mobility european Contract ERB CHRXCT930344.

[1] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

[2] A. Dalgarno and W. D. Davidson, Adv. At. Mol. Phys. **2**, 1 (1966).

[3] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, Science **269**, 198 (1995).

[4] C. C. Bradley, C. A. Sackett, J. J. Tollett, and R. G. Hulet, Phys. Rev. Lett. **75**, 168 (1995).

[5] H. R. Thorsheim, J. Weiner, and P. S. Julienne, Phys. Rev. Lett. **58**, 2420 (1987).

[6] H. Knöckel, T. Johr, H. Richter, and E. Tiemann, Chem. Phys. **152**, 399 (1991).

[7] E. R. I. Abraham, W. I. McAlexander, C. A. Sackett, and R. G. Hulet, Phys. Rev. Lett. **74**, 1315 (1995); E. R. I. Abraham, N. W. M. Richtie, W. I. McAlexander, and R. G. Hulet, J. Chem. Phys. **103**, 7773 (1995).

[8] L. P. Ratliff, M. E. Waghsul, P. D. Lett, S. L. Rolston, and W. D. Phillips, J. Chem. Phys. **101**, 2638 (1994).

[9] J. D. Miller, R. A. Cline, and D. J. Heinzen, Phys. Rev. Lett. **71**, 2204 (1993).

[10] B. Bussery and M. Aubert-Frécon, J. Chem. Phys. **82**, 3224 (1985).

[11] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995).

[12] P. Lett (private communication); P. D. Lett, P. S. Julienne, and W. D. Phillips, Annu. Rev. Phys. Chem. **46**, 423 (1995).

[13] P. van der Straaten (private communication).

[14] O. Dulieu, S. Magnier, and F. Masnou-Seeuws, Z. Phys. D **32**, 229 (1994).

[15] E. E. Nikitin and B. M. Smirnov, Sov. Phys. Usp. **21**, 95 (1978).

[16] T. M. Kereselidze and M. Chibisov, Sov. Phys. JETP **41**, 6 (1975).

[17] S. Magnier, M. Aubert-Frécon, O. Bouty, F. Masnou-Seeuws, Ph. Millié, and V. N. Ostrovsky, J. Phys. B **27**, 1723 (1994).

[18] H. Lefebvre-Brion and R. W. Field, in *Perturbations in the Spectra of Diatomic Molecules* (Academic Press, London, 1986).

[19] S. Magnier, Ph. Millié, O. Dulieu, and F. Masnou-Seeuws, J. Chem. Phys. **98**, 7113 (1993).

[20] S. Magnier and Ph. Millié, Phys. Rev. A (to be published).

[21] M. Foucrault, Ph. Millié, and J. P. Daudey, J. Chem. Phys. **96**, 1257 (1992).

[22] B. Lévy, *Current Aspects of Quantum Chemistry,* Studies in Physical and Theoretical Chemistry, (Elsevier, New York, 1981), Vol. 121, p. 127.

[23] M. C. Bacchus-Montabonel, G. Chambaud, B. Lévy, and Ph. Millié, J. Chim. Phys. **80**, 3 (1983).

[24] P. O. Lowdin, J. Chem. Phys. **18**, 365 (1950).

[25] C. Angeli, M. Persico, M. Allegrini, G. de Filippo, F. Fuso, D. Gruber, L. Windholz, and M. Musso, J. Chem. Phys. **102**, 7782 (1995).

[26] W. Meyer (private communication).

[27] J. L. Krause and R. S. Berry, Comments At. Mol. Phys. **18**, 91 (1986).

[28] P. Kowalczyk, Chem. Phys. Lett. **68**, 203 (1979); P. Kowalczyk, J. Phys. B **17**, 817 (1984).

[29] R. W. Heather and P. S. Julienne, Phys. Rev. A **47**, 1887 (1993).

[30] M. Krauss and W. Stevens, J. Chem. Phys. **93**, 4236 (1990).