PHYSICAL REVIEW A VOLUME 56, NUMBER 3 SEPTEMBER 1997

Electron capture in collisions of H^+ ions with S atoms and its reverse process below kilo-electron-volt energies

M. Kimura
School of Allied Health Sciences, Yamaguchi University, Ube, Yamaguchi 755, Japan and Institute of Space and Astronautical Science, Yoshinodai, Sagamihara 229, Japan

J.-P. Gu, G. Hirsch, and R. J. Buenker
Theoretische Chemie, Bergische Universität-Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany

A. Domondon and T. Watanabe
Department of Physics, International Christian University, Tokyo, Japan

H. Sato
Department of Information Science, Ochanomizu University, Tokyo, Japan

(Received 6 March 1997)

Electron capture in $H^++S(^3P,^1D)$ collisions is studied theoretically by using a semiclassical molecular representation with five molecular channels from the initial ground and excited states at collision energies above 10 eV. Electron capture in S^+ $(^4S)+H(1\,s)$ collisions is also investigated by using three molecular channels in order to assess the earlier estimation which gave the rate constant of 10^{-15} cm^3/s at 10^4 K for the process. The *ab initio* potential curves and nonadiabatic coupling matrix elements for the HS^+ system are obtained from multireference single- and double-excitation configuration-interaction calculations employing relatively large basis sets. Dominant capture channels corresponding to the $[H+S^+(^2P)]$ and $[H+S^+(^2D)]$ states lie lower by 0.2 and 1.4 eV, and 1.34 and 2.5 eV from the initial ground $[H^++S(^3P)]$ and excited $[H^++S(^1D)]$ states, respectively. The present results show that electron capture from the excited species is found to be rather weak at lower energies. But it rapidly becomes comparable to that from the ground state. Electron capture in S^+ $(^4S)+H$ collisions proceeds through the two-step mechanism at lower energies, and therefore, the cross section is found to be small with the value less than 10^{-17} cm^2 below 1 keV, thus supporting the earlier estimation. [S1050-2947(97)05808-3]

PACS number(s): 34.10.+x, 34.70.+e, 34.20.−b

I. INTRODUCTION

The distribution of ionic states of atomic elements provides important information for the diagnosis of the ionic structure in the interstellar gas, solar corona, and planetary nebulae [1]. It is also essential in designing and operating controlled thermonuclear fusion devices based on confined hot plasma [2]. Standard models which describe forbidden lines of neutral carbon and sulfur underestimate the intensities of the observed [C I] and [S I] lines, and it has been proposed that inclusion in the models of charge-transfer reactions with atomic hydrogen may account for some parts of the discrepancies [3]; i.e., (i) the ground atom:

$$H^++S(^3P)\rightarrow H+S^+(^2P)+0.198\ \text{eV} \tag{1a}$$

$$\rightarrow H+S^+(^2D)+1.397\ \text{eV}, \tag{1b}$$

(ii) the excited atom:

$$H^++S(^1D)\rightarrow H+S^+(^2P)+1.343\ \text{eV} \tag{2a}$$

$$\rightarrow H+S^+(^2D)+2.542\ \text{eV}, \tag{2b}$$

and (iii) the capture by S^+ ions:

$$S^+(^4S)+H\rightarrow S(^3P)+H^+-3.238\ \text{eV} \tag{3}$$

Butler and Dalgarno [4] estimated the capture rate coefficient by scaling the result of the $[C^++H]$ system at a temperature of 1×10^4 K and found that the process is slow with a rate coefficient of the order of less than 10^{-15} cm^3/s in connection to the forbidden-line spectrum analysis in the astrophysical environment. On the other hand, Eichler, Tsuji, and Ishihara [5] calculated charge-transfer cross sections of the above process in the collision energy range from 40 keV–1000 keV by using the Oppenheimer-Brinkman-Kramers approximation, and found good agreement with experimental data at higher energies by Goffe, Sha, and Gilbody [6]. To the best of our knowledge, there is no rigorous experimental attempt to study the capture process of this system at low to intermediate energies, and capture cross sections are needed urgently.

In this paper, we perform a study for electron capture in all the above processes by using a molecular-orbital expansion method within a semiclassical framework. Process (3) is of astrophysical importance as clearly exemplified in Ref. [4] and hence, we also evaluate the magnitude of the cross section. We have examined the final distribution of the S^+ ionic states in all the above processes as well.

II. THEORETICAL MODEL

The present SH^+ calculations are an extension of our earlier work on the SiH^+ system reported [7] for the determina-

TABLE I. Number of reference configurations, N_{ref}, and number of roots N_{root}, treated in each irreducible representation and the corresponding number of generated (N_{tot}) and selected (N_{sel}) symmetry-adapted functions for a threshold of 1.5×10^{-6} E_h at an S-H internuclear distance of $2.6a_0$.

State	$N_{\mathrm{ref}}/N_{\mathrm{root}}$	N_{tot}	N_{sel}
$^1A_1$	160/6	599 500	17 645
$^1B_1$	100/4	519 496	17 162
$^1A_2$	112/4	572 701	17 287
$^3A_1$	150/3	978 443	19 588
$^3B_1$	107/4	769 847	19 366
$^3A_2$	107/5	960 929	19 779
$^5A_2$	67/2	401 745	9 066

tion of molecular electronic states. For collision dynamics, a semiclassical close-coupling method has been used extensively by this group [8–10] and others [11], and hence, only a short summary of electronic-state and collision dynamics calculations should be sufficient and is given here [12].

A. Molecular states and couplings

In the present *ab initio* calculations, the atomic orbital basis set employed for the sulfur atom is $(12s9p)$, contracted to $[6s5p]$ [13], augmented by two d and one f polarization functions. This basis set, furthermore, includes s-, p-, and d-type Rydberg functions with exponents 0.023, 0.020, and 0.015 [14], respectively, to give the final $[7s6p3d1f]$ contracted basis set. For the hydrogen atom, we employ the same $(7s3p)/[5s3p]$ basis set which was used in Ref. [15], but we add one six-component d-type function with an exponent of 1.0. The potential curves are obtained by the multireference single- and double-excitation (MRDCI) configuration-interaction method [16], with configuration selection and energy extrapolation using the Table CI algorithm [17]. In the CI calculations, the five lowest molecular orbitals (MOs) are always doubly occupied, whereas the five highest ones are discarded. A selection threshold [16] of 1.5×10^{-6} hartree has been used in the present treatment. The potential curves of each state have been calculated at more than 40 different internuclear distances from 2.0–12.0. a.u. Other details of the present MRDCI calculations are shown in Table I.

B. Collision dynamics

A semiclassical MO expansion method with a straight-line trajectory of the incident ion was employed to study the collision dynamics below 10 keV [12]. In this approach, the relative motion of heavy particles is treated classically, while electronic motions are treated quantum mechanically. The total scattering wave function was expanded in terms of products of a molecular electronic state and atomic-type electron translation factors (ETFs), in which the inclusion of the ETF satisfies the correct scattering boundary condition. Substituting the total wave function into the time-dependent Schrödinger equation, and retaining the ETF correction up to the first order in the relative velocity between the collision partners, we obtain a set of first-order coupled equations in time t. Transitions between the molecular states are driven by nonadiabatic couplings. By solving the coupled equations numerically, we obtain the scattering amplitudes for transitions: the square of the amplitude gives the transition probability, and integration of the probability over the impact parameter gives the cross section. The molecular states included in the dynamical calculations are the three sets of states shown in Fig. 1: (i) triplets; $[\mathrm{H}+\mathrm{S}^+(^2P)]$ $(1\,^3\Sigma^+,2\,^3\Pi)$ and $[\mathrm{H}+\mathrm{S}^+(^2D)]$ $(2\,^3\Sigma^-,1\,^3\Pi)$ states for electron capture from the initial ground $[\mathrm{H}^++\mathrm{S}(^3P)]$ $(3\,^3\Sigma^-,3\,^3\Pi)$ states, (ii) singlets; $[\mathrm{H}+\mathrm{S}^+(^2P)]$ $(1\,^1\Sigma^+,2\,^1\Pi)$ and $[\mathrm{H}+\mathrm{S}^+(^2D)]$ $(1\,^1\Pi)$ states for electron capture from the initial excited $[\mathrm{H}^++\mathrm{S}(^1D)]$ $(2\,^1\Sigma^+,3\,^1\Pi)$ states, and (iii) the molecular states included for the $[\mathrm{H}+\mathrm{S}^+(^4S)]$ collision system are: $[\mathrm{H}+\mathrm{S}^+(^4S)]$ $(1\,^3\Sigma^-)$ for the initial, and $[\mathrm{H}^++\mathrm{S}(^3P)]$ $(3\,^3\Sigma^-)$ state for charge transfer and $[\mathrm{H}+\mathrm{S}^+(^2D)]$ $(2\,^3\Sigma^-)$ state for excitation.

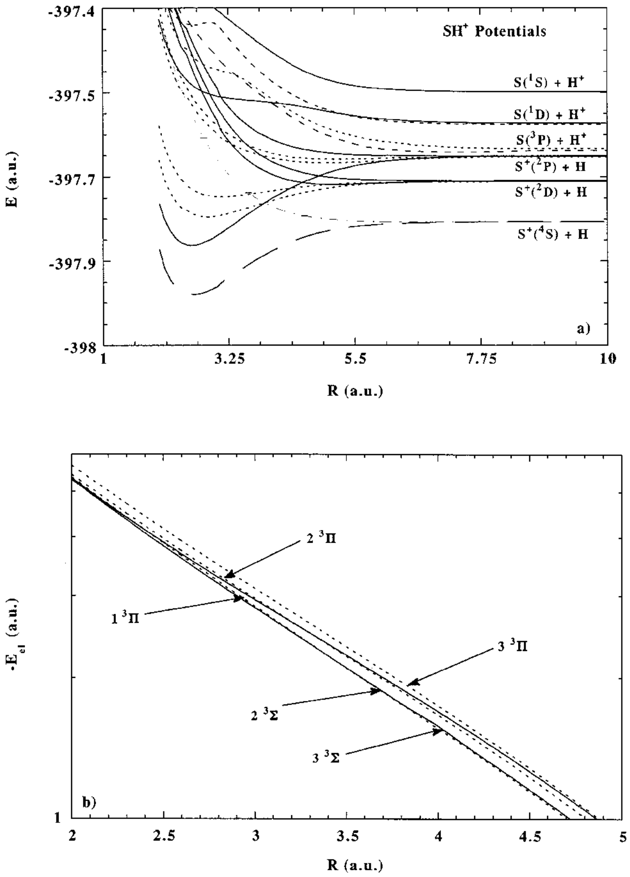

FIG. 1. (a) Adiabatic potentials of the SH^+ system (Δ states are not included), and (b) adiabatic potentials (in log scale) after subtracting the Coulomb repulsion term and being measured from 397.0 a.u. Here we present only those Σ and Π states in the triplets used in the calculations at small R.

III. RESULTS

A. Adiabatic potentials and coupling matrix elements

The calculated adiabatic potentials are shown in Fig. 1(a) from the lowest channel to a few excited manifolds. Only those potentials used in the calculation are enlarged in Fig. 1(b) (after subtracting the Coulomb term) to exemplify features of the potentials at small internuclear separation. The initial $[\mathrm{H}^++\mathrm{S}(^3P)]$ channel lies very close to the electron

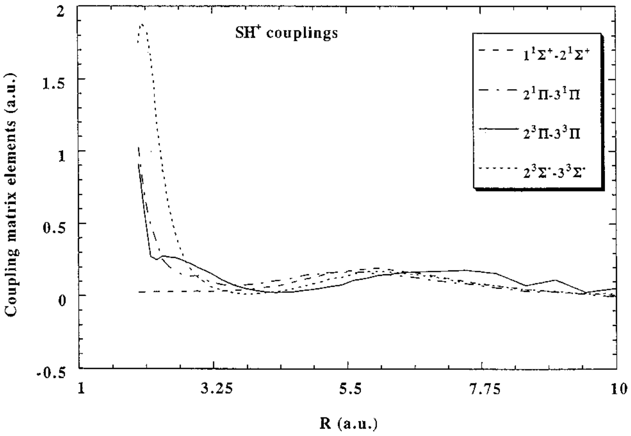

FIG. 2. Representative radial coupling matrix elements for the SH$^+$ system.

capture $[\mathrm{H}+\mathrm{S}^+(^2P)]$ channel with an asymptotic energy defect of 0.2 eV, followed by the electron capture $[\mathrm{H}+\mathrm{S}^+(^2D)]$ channel with an asymptotic energy of 1.4 eV. Therefore, from a simple argument of the energy defect and the number of states available in capture channels, electron capture to the $[\mathrm{H}+\mathrm{S}^+(^2P)]$ channel may become dominant at low energy, while the $[\mathrm{H}+\mathrm{S}^+(^2D)]$ channel is expected to take over at higher energies. The initial excited $[\mathrm{H}^++\mathrm{S}(^1D)]$ channel lies higher by 2.542 eV than the charge transfer $[\mathrm{H}+\mathrm{S}^+(^2D)]$ channel and electron capture from this initial channel should be weak, particularly at lower energies below 1.0 keV. Both processes are exothermic and have no thresholds. The $1\,^5\Sigma^-$ potential, correlating to the $[\mathrm{H}+\mathrm{S}^+(^4S)]$ state, crosses within $R<4$ a.u. with a series of spin-changing triplet states, and therefore, at very low collision energy, spin-changing processes through a spin-orbit coupling mechanism among these states might become important for the energy-balance analysis in an astrophysical environment. Our confidence level in the precision in the present calculation is believed to be within 500 cm^{-1}, which is appropriate for the present purpose.

Representative radial coupling matrix elements are displayed in Fig. 2. For the triplet manifold, the $2\,^3\Sigma^- - 3\,^3\Sigma^-$ radial coupling matrix element possesses a large peak near $R=2.05$ a.u., and is dominant for the transition at lower energies. As the energy increases, this strong coupling becomes more diabatic in nature and is expected to be less effective. The radial coupling which connects between $1\,^3\Sigma^- - 3\,^3\Sigma^-$ is rather weak, and the direct transition from $1\,^3\Sigma^- - 3\,^3\Sigma^-$ is unlikely, at least at low energies, and the two-step mechanism should dominate. At higher energies, $2\,^3\Pi - 3\,^3\Pi$ coupling is expected to begin to dominate. For the singlets, Π-Π coupling is slightly stronger at R smaller than 3 a.u., and is considered to be effective for the $\mathrm{S}^+(^2P)$ population. Other radial couplings are found to be weak, while rotational couplings among these corresponding states are of medium strength.

B. Charge transfer from the ground S(^3P) atoms

The spin-averaged electron-capture cross section from the ground S(^3P) atoms by H$^+$ impact is illustrated in Fig. 3(a). A few interesting features are seen including: (i) both electron-capture cross sections to the $[\mathrm{H}+\mathrm{S}^+(^2P)]$ and $[\mathrm{H}+\mathrm{S}^+(^2D)]$ states increasing rapidly as the collision energy increases from 10 eV, with a slightly larger magnitude for the $[\mathrm{H}+\mathrm{S}^+(^2P)]$ formation, (ii) the cross sections to these two states show slight out-of-phase oscillatory structures at intermediate energies from 30 eV–2 keV region, indicating rather strong interference between these two channels, (iii) above 3 keV, the electron capture to $[\mathrm{H}+\mathrm{S}^+(^2D)]$ becomes dominant in magnitude over that of $[\mathrm{H}+\mathrm{S}^+(^2P)]$, even though the asymptotic energy defect is larger. This is because the Σ-Σ radial coupling between the initial and $2\,^3\Sigma^-$ state becomes more effective in this energy domain, resulting in a larger flux population in the Σ state, and (iv) the $[\mathrm{H}+\mathrm{S}^+(^2P)]$ state formation begins to show a slight decrease beyond $E=2$ keV because of the less effective Π-Π radial coupling being the sole driving force in this energy region. Between 0.2 and 1.0 keV, both cross sections are similar in magnitude and energy dependence, causing a strong mixing between the two channels, and their magnitudes are found to exceed the value of 10^{-16} cm^2.

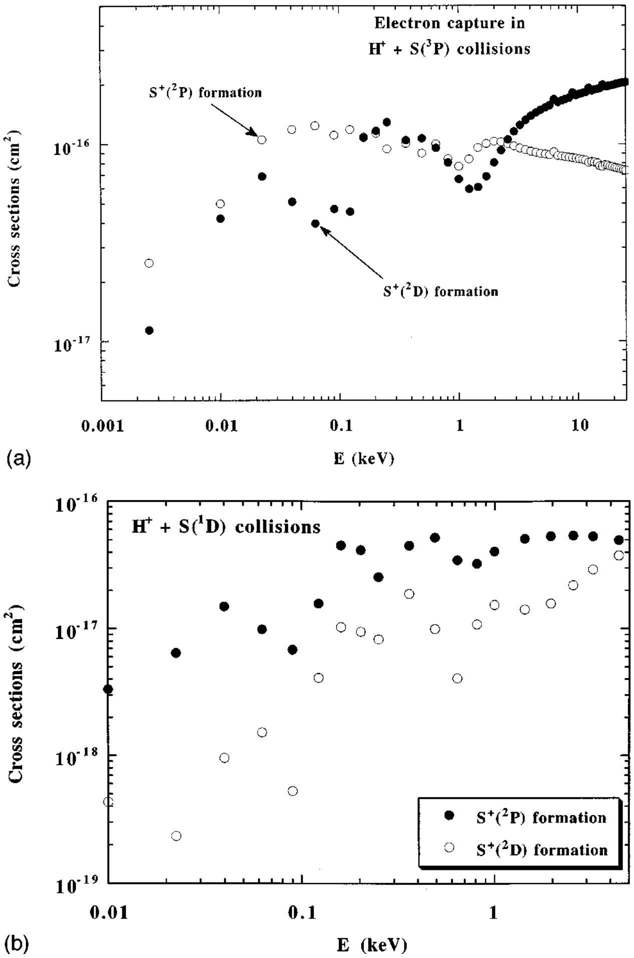

FIG. 3. Electron capture cross sections for (a) H$^+$+S(^3P) collisions below 30 keV, and for (b) H$^+$+S(^1D) collisions.

C. Charge transfer from the excited S(^1D) atoms

The electron-capture cross section from the excited S(^1D) atoms by H$^+$ impact is displayed in Fig. 3(b). Since our main aim in this study is to estimate the order of the cross section, many points of the cross section with finer energy mesh have not been calculated. Due to larger energy

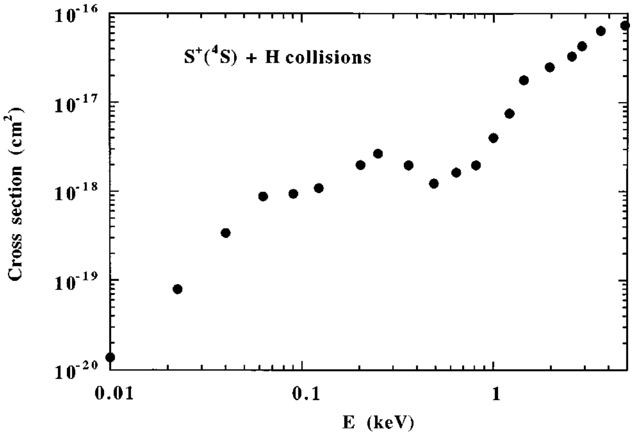

FIG. 4. Electron-capture cross sections for S$^+$(^{4}S)+H collisions.

defects from the initial channel, the electron capture for [H+S$^+$(^2P)] and [H+S$^+$(^2D)] formations are smaller in size than those from the ground state at energies below 0.1 keV, with the much smaller value for the S$^+$(^2D) formation. Contrary to that of the ground state, the cross section for the [H+S$^+$(^2P)] formation is larger than that for the [H+S$^+$(^2D)] formation at all energies studied because of the smaller energy defect and a more effective coupling scheme. For the [H+S$^+$(^2P)] formation, the Σ and Π states contribute equally to electron capture above 0.5 keV, while below this energy, the Π state contribution is dominant, which may be apparent from dynamical considerations. Weak oscillatory structures, some out-of-phase and in-phase, are seen between the two cross sections, indicating the strong interference between these two channels with a strong energy dependence. Both cross sections are smaller in magnitude than those in the ground state in all energies, but reach their maxima at around 6 keV, with the value of 5×10^{-17} cm^2. This observation may be useful for the astrophysical analysis in the interstellar environment. The difference between the cross sections for the two processes widens below 0.1 keV by an order of magnitude.

D. Charge transfer in S$^+$(^4S)+H collisions

The present electron-capture cross sections by S$^+$ ion impact on H atoms are displayed in Fig. 4. Butler and Dalgarno [4] have estimated the rate coefficient for the process based on the scaling from C$^+$+H collisions, and found it to be very small, with a value less than 10^{-15} cm^3/s at 10 000 K. The mechanism for electron capture was examined based on using three MO states corresponding to [S$^+$(^4S)+H], [S$^+$(^2D)+H], and [H$^+$+S(^3P)] states. Unlike the initial state, the other two states possess a Π component, and therefore, there are rotational couplings with the initial state. However, we have found that its effect is not as large as that of the radial coupling in the low-energy part of this study, and have ignored it. The process is endothermic, and has a threshold of 3.24 eV as in Eq. (3). The initial [S$^+$(^4S) +H], and excited [S$^+$(^2D)+H] states are found to have very weak mixing of the states in all regions of R, and correspondingly, a very weak coupling. In addition, the direct-capture coupling to the [H$^+$+S(^3P)] state from the initial state is also found to be very weak. Although the radial coupling between the [S$^+$(^2D)+H], and [H$^+$+S(^3P)] states are strong in the small R region as seen above, the entire process proceeds as a two-step mechanism, and is not considered to be so effective, at least, at lower energies. The result increases rapidly from the threshold, but the magnitude is small with a value of less than 10^{-20} cm^2 at the lowest energy studied. It approaches the neighborhood of 10^{-17} cm^2 above 1 keV. As Butler and Dalgarno speculated, the process is slow and causes a minor effect for analysis of the forbidden spectrum lines. However, as shown in Fig. 4, the cross section continues to increase with increasing energy and above a few keV, it may reach the neighborhood of 10^{-16} cm^2 and is no longer a negligible process. As stated above, in this calculation, we have neglected the capture process from the initial $^5\Sigma^-$ state. However, at low energy where the contribution from the initial $^3\Sigma^-$ state is negligible, the capture from the initial $^5\Sigma^-$ state is expected to become dominant through spin-orbit coupling.

IV. CONCLUSION

We have studied electron capture in collisions of S(^3P) atoms with H$^+$ ions below 10 keV, and found that the process is very effective and the cross sections for S$^+$(^2P,^2D) formation reach as large as $\sim10^{-16}$ cm^2 above 30 eV. We have also investigated electron capture from excited S(^1D) atoms by H$^+$ ion impact in the same energy range and found that the magnitude of the cross sections for S$^+$(^2P,^2D) formation shows a gradually increasing trend compared to that for the ground-state atom in all energies and reaches values larger than 10^{-16} cm^2 at the highest energy. It rapidly decreases as the collision energy decreases and becomes less than 10^{-17} cm^2 below 50 eV. Electron capture for the collisions of S$^+$(^4S) ions with H atoms has also been examined to calculate the cross sections, and it is found that the reaction is very slow with the value less than 10^{-17} cm^2 below 1 keV. Our rough estimation of the rate coefficient based on these cross sections reveals that the rate is indeed very slow with a value of less than 10^{-15} cm^3/s at 10 000 K, consistent with the estimate of Butler and Dalgarno.

ACKNOWLEDGMENTS

This work was supported in part by the Deutsche Forschungsgemeinschaft in the form of a Forschergruppe and Grant No. Bu 450/7-1 (J.P.G., G.H., R.J.B.). The financial support of the Fonds der Chemischen Industrie is also hereby gratefully acknowledged. M.K. also acknowledges financial support from the National Science Foundation through the Institute of Theoretical Atomic and Molecular Physics (ITAMP) Smithsonian Center for Astrophysics when this project was initiated. The authors thank Professor A. Dalgarno for a useful discussion.

[1] J. B. Kingdon and G. J. Ferland, Astrophys. J. Suppl. Ser. **106**, 205 (1996).

[2] J. W. Gallagher, B. H. Bransden, and R. K. Janev, J. Phys. Chem. Ref. Data **12**, 873 (1983).

[3] D. Pequignot, S. M. V. Aldrovani, and G. Stasinska, Astron. Astrophys. **58**, 411 (1978).

[4] S. E. Butler and A. Dalgarno, Astron. Astrophys. **85**, 144 (1980).

[5] J. K. M. Eichler, A. Tsuji, and T. Ishihara, Phys. Rev. A **23**, 2833 (1980).

[6] T. V. Goffe, M. B. Sha, and H. B. Gilbody, J. Phys. B **12**, 3763 (1979).

[7] A. B. Sannigrahi, R. J. Buenker, G. Hirsch, and J.-P. Gu, Chem. Phys. Lett. **237**, 204 (1995).

[8] M. Kimura, J. P. Gu, H. P. Liebermann, Y. Li, G. Hirsch, R. J. Buenker, and A. Dalgarno, Phys. Rev. A **50**, 4854 (1994).

[9] M. Kimura, J. P. Gu, Y. Li, G. Hirsch, and R. J. Buenker, Phys. Rev. A **49**, 3131 (1994).

[10] M. Kimura, J. P. Gu, G. Hirsch, and R. J. Buenker, Phys. Rev. A **51**, 2063 (1995).

[11] T. G. Heil, S. E. Butler, and A. Dalgarono, Phys. Rev. A **23**, 1100 (1981).

[12] M. Kimura and N. F. Lane, in *Advances in Atomic and Molecular Optical Physics*, edited by D. R. Bates and B. Bederson (Academic Press, New York, 1989), Vol. 26, p. 76.

[13] A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).

[14] T. H. Dunning, Jr. and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977).

[15] J. Roemelt, S. D. Peyerimhoff, and R. J. Buenker, Chem. Phys. **34**, 403 (1978).

[16] R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974); **39**, 217 (1975); R. J. Buenker, Int. J. Quantum Chem. **29**, 435 (1986).

[17] R. J. Buenker, in *Proceedings of the Workshop on Quantum Chemistry and Molecular Physics, Wollongong, Australia*, edited by P. G. Burton (University Press, Wollongong, 1980); in *Studies in Physical and Theoretical Chemistry*, edited by R. Carbo, Current Aspects of Quantum Chemistry (Elsevier, Amsterdam, 1981), Vol. 21, p. 17; R. J. Buenker and R. A. Phillips, J. Mol. Struct. Theochem. **123**, 291 (1985).