PHYSICAL REVIEW A **89**, 062711 (2014)

Theoretical prediction of the binding of a positron to a formaldehyde molecule using a first-principles calculation

Yurika Yamada, Yukiumi Kita,* and Masanori Tachikawa†
Quantum Chemistry Division, Yokohama City University, Seto 22-2, Kanazawa-ku, Yokohama 236-0027, Japan

(Received 6 February 2014; published 16 June 2014)

The vertical positron affinity (PA) value at the equilibrium position of a formaldehyde molecule is predicted as +25(3) meV with the highly accurate quantum Monte Carlo method. Applying anharmonic vibrational analysis, we have found that the vibrational excitation of the $C = O$ stretching mode drastically enhances the PA value, due to the increment of the molecular dipole moment along this mode. Our predictions of the vibrational averaged PA values at the fundamental and overtone states are 31 and 36 meV, respectively, which strongly supports the conclusion that a positron can bind to formaldehyde.

DOI: 10.1103/PhysRevA.89.062711 PACS number(s): 34.80.−i, 31.15.A−

The positron is studied in many areas such as physics, chemistry, materials science, medicine, and their interdisciplinary areas [1–3]. Recently, Surko and co-workers [4–10] experimentally measured positron affinity (PA) values, binding energies of a positron to atoms or molecules, for a number of molecular species via the vibrational Feshbach resonance (VFR) technique, in which a positron-molecular complex can be formed at the molecular vibrational excited states by absorbing the excess energy of an incident positron. The understanding of positron attachment processes is expected to provide useful information for the interaction of the positron with surfaces, bulk materials, and polymers, as investigated using techniques such as Doppler broadening of positron annihilation radiation (DBAR), angular correlation of annihilation radiation (ACAR), and positron annihilation lifetime spectroscopy (PALS) [11,12].

Formaldehyde (CH_2O) is the fundamental organic compound containing the important carbonyl ($C = O$) functional group with its strong permanent dipole moment of 2.339(13) D [13], which is greater than the critical threshold value of 1.625 D for positron binding, theoretically proved by Crawford and several other authors [14,15]. The $C = O$ functional group is a ubiquitous building block of chemical compounds including polymers such as poly(methyl methacrylate), polyethylene terephthalate, and polycarbonate, for which positron radiation experiments have been reported recently [16,17]. For these reasons, this molecule is an excellent candidate species for not only a benchmark of theoretical developments [18,19], but also the understanding of the fundamental contribution of the $C = O$ group in positron radiation measurements. Even though there have been recent experimental reports for positron-CH_2O scattering [20] or positron binding to another carbonyl and aldehyde species such as acetone and acetaldehyde [8], there is a need for more experimental investigations into the binding of a positron to a formaldehyde molecule. For polyatomic molecules, PAs were also theoretically evaluated with the configuration interaction (CI) method [18,19]. Such small CI calculations, however, significantly underestimate PA compared with the experimental one, because of insufficient recovery of the positron-electron correlation contribution. Furthermore, these PA calculations are employed only at their equilibrium geometry, and one often ignores the effect of molecular vibration which should be indispensable in reproducing the experimental condition in the theoretical treatment.

In this paper, thus, we would like to focus on the binding of a positron to the formaldehyde molecule with the state-of-the-art first-principles quantum Monte Carlo (QMC) method combined with CI approaches, including all the degrees of vibrational contribution as well as quantum-mechanical positron and electrons. Here, two types of PA values are accurately evaluated: (i) a *vertical* PA value at the equilibrium geometry, and (ii) a *vibrational averaged* PA value including anharmonic molecular vibrational effects. We will quantitatively predict the PA value of the formaldehyde molecule, which can be regarded as a milestone for further experimental development.

The vertical PA value is directly calculated by the energy difference between the total energies of a parent molecule (X) and its positron-molecular complex (denoted by $[X;e^+]$) as $\mathrm{PA} \equiv E^X - E^{[X;e^+]}$ at a given geometry of the parent molecule. Two successful theoretical approaches are known for evaluating the accurate vertical PA value of polyatomic molecules: diffusion Monte Carlo (DMC) calculations [21–25] and variational calculations using the explicitly correlated Gaussian (ECG) basis set [26–29]. The ECG calculations cannot in practice be applied to large systems because the required computational effort grows very rapidly with the number of particles. Thus, we employed the DMC method for the vertical PA calculation of the CH_2O molecule. The equilibrium geometry of CH_2O was optimized by a coupled-cluster singles and doubles (CCSD) level with Dunning's augmented correlation consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set. The DMC calculations were performed for the ground-state energies of CH_2O and $[CH_2O;e^+]$ systems at this equilibrium geometry using the CASINO code [30]. The Slater-Jastrow type function was used as the trial wave function for both systems, where the Slater part of the function was obtained at the Hartree-Fock (HF) level of multicomponent molecular orbital (MCMO) theory [31–33] in which the molecular orbital of the positron is obtained in a similar fashion to the conventional HF method, with the electronic and positronic orbitals being expanded as a linear combination of atomic orbitals [34]. The Jastrow part of the function contains two- and three-body terms including electron-electron, electron-positron, electron-nucleus, positron-nucleus, and electron-electron-nucleus

---

*ykita@yokohama-cu.ac.jp
†tachi@yokohama-cu.ac.jp

©2014 American Physical Society

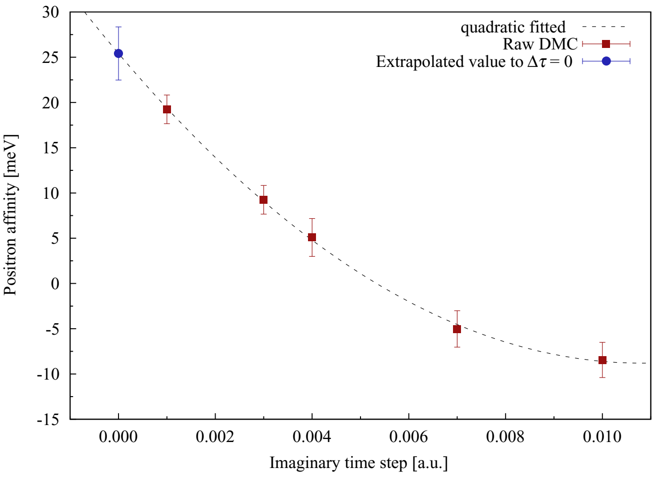

FIG. 1. (Color online) The imaginary time-step dependence of the PA of the CH_2O molecule. The dashed line means a quadratic fitted function for DMC data at each time step. The extrapolated PA value to zero time step is shown by the blue circle.

terms, where the total numbers of variational parameters are 87 and 107 for CH_2O and $[CH_2O;e^+]$, respectively. In DMC calculations, the target population of walkers was chosen to be 9600 for both systems. These numbers are sufficient to make the population control error completely negligible. The total energies were calculated with five imaginary time steps ($\Delta\tau$) ranging from 0.001 to 0.010 a.u. To remove the finite time-step error, the total energy was estimated by extrapolating DMC energies at each finite time step to zero time step. Figure 1 shows the imaginary time-step dependence of the PA value in the DMC calculation. The variation of the PA with time step is significant in this molecule, and the PA values at the large time step (0.007 and 0.010 a.u.) are negative, suggesting that the CH_2O molecule does not bind a positron. The variation of the PA values with respect to each time step is, however, quite smooth, and the PA can readily be extrapolated to zero time step.

The final PA value at the zero time step with the DMC method was estimated as 25(3) meV, where the total energies of CH_2O and $[CH_2O;e^+]$ species are −114.476 84(8) and −114.477 81(7) hartrees, respectively. Our PA value is about 40% larger than the previous CI value of 18.6 meV by Strasburger [18] due to the accurate estimation of correlation energies in DMC calculations. Since our DMC calculations yield very low variational energy for CH_2O and $[CH_2O;e^+]$, our vertical PA value of CH_2O with DMC calculation can be regarded as a highly accurate and reliable value at the present stage. We address here that the DMC method is variational in the sense that the DMC energy is always higher than the exact energy.

To estimate the PA value including the effect of molecular vibrations of the CH_2O molecule, we employed the vibrational averaged scheme proposed by Gianturco *et al.* [35]. In their scheme, the PA of a parent molecule at various vibrational states is assumed to be evaluated in the Born-Oppenheimer framework—that is, within the picture of an immediate positron attachment to molecule at a given geometry—and be modulated by the vibrational wave function of a parent molecule before the geometrical relaxation process due to the positron attachment occurs. Under this assumption, the vibrational averaged PA value (PA_v) is defined as

$$\mathrm{PA}_v = \frac{\int \mathrm{PA}\,(\boldsymbol{Q})\,|\psi_v\,(\boldsymbol{Q})|^2\,d\boldsymbol{Q}}{\int |\psi_v\,(\boldsymbol{Q})|^2\,d\boldsymbol{Q}}, \tag{1}$$

where $\boldsymbol{Q} = (q_1,q_2,\ldots)$ is a set of vibrational normal coordinates, ψ_v the vibrational wave function of the vth state, $\mathrm{PA}\,(\boldsymbol{Q})$ a vertical PA value at a given molecular geometry $\boldsymbol{Q}$, and we assumed the negative PA values as zero during the numerical integration of Eq. (1).

TABLE I. The harmonic vibrational frequencies and IR intensities of six normal vibrational modes of CH_2O molecule.

Mode type	Frequency (cm^{-1})	IR intensity ($km\ mol^{-1}$)
1 Symmetric C–H stretching	2962	58.0
2 C = O stretching	1816	85.6
3 CH_2 bending	1548	11.7
4 Out-of-plane bending	1205	6.6
5 Antisymmetric C–H stretching	3032	85.9
6 CH_2 rocking	1279	12.0

Table I shows harmonic vibrational frequencies and infrared radiation (IR) intensities for six vibrational normal coordinates of the CH_2O molecule at the CCSD/aug-cc-pVTZ level of calculation. The IR intensities of the symmetric C–H stretching (mode 1), C = O stretching (mode 2), and antisymmetric C–H stretching (mode 5) modes are relatively larger than those of other modes. Based on the theoretical prediction by Crawford [14], it is strongly expected that vibrational excitations of these modes give larger PA variations compared to those of other modes, because IR intensity is proportional to the square of the derivative of the dipole moment with respect to the corresponding normal mode coordinate.

In order to calculate PA_v values, a *global surface* of PA values $[\mathrm{PA}(\boldsymbol{Q})]$ leading to a number of the vertical PA calculations in the whole vibrational configuration space is required. Since a time-consuming DMC calculation is not realistic for such global PA surface due to the limitation of our computational facilities, we employed the less time-consuming CI calculation including electronic single excitation, positronic single excitation, and double excitations of single-electronic–single-positronic excitation configurations (CISDs). A truncated CI calculation generally gives poor PA values compared to the DMC calculation, but our CISD calculation with *well-chosen* basis sets [36] can quantitatively reproduce the DMC value. The vertical PA value at the equilibrium geometry with our CISD calculation is 25.26 meV, which is within the error of the DMC value of 25(3) meV.

The vibrational wave function of the CH_2O molecule was solved using a Watson Hamiltonian [37] including rotation-vibration couplings. The global potential energy surface (PES) in the Hamiltonian is expressed by a table of potential energy values at grid points in vibrational configuration space, and is calculated by interpolating them with the spline interpolation technique as required. In principles, a six-dimensional PES is required for a CH_2O molecule, but high-dimensional couplings

($\geqslant 4$) in PES generally give negligible contributions despite tremendous computational efforts. An efficient way to reduce high-dimensional couplings has been proposed by Carter *et al.* [38] referred to as n-mode representation. In this method, a potential energy function is expanded by the number of couplings between normal mode coordinates, and then the approximate PES is expressed by truncating higher-order coupling terms. To construct an approximate PES for CH_2O molecule, we employed the three-mode representation including coupling terms up to third order. The potential energy values for each grid point are calculated with the CCSD/aug-cc-pVTZ level of calculation, where the total number of grid points is 33 476.

To obtain vibrational wave functions, we employed a vibrational self-consistent (VSCF) theory [39] based on a mean-field approximation. In VSCF theory, a total vibrational wave function (ψ_v^{VSCF}) of a given state is expressed by products of *modal* wave functions ($\varphi_{v_i}^{(i)}$) as $\psi_v^{\mathrm{VSCF}}(\boldsymbol{Q}) = \prod_i \varphi_{v_i}^{(i)}(q_i)$, where $\boldsymbol{v} = (v_1, v_2, \ldots)$ is a set of vibrational quantum numbers of modals. A modal wave function is generally expanded as a linear combination of eigenfunctions of the harmonic oscillator ($\phi_n^{(i)}$) as $\varphi_{v_i}^{(i)}(q_i) = \sum_{n=} c_n^{(i)} \phi_n^{(i)}(q_i; \varepsilon^{(i)}, Q_{\mathrm{C}}^{(i)})$, where the expansion coefficients $\{c_n^{(i)}\}$, exponents $\{\varepsilon^{(i)}\}$, and centers $\{Q_{\mathrm{C}}^{(i)}\}$ in basis functions are variational parameters. To optimize these parameters, we employed the linear optimization scheme proposed by Toulouse and Umrigar [40] together with a variational Monte Carlo (VMC) technique [41]. Vibrational wave functions were optimized for states satisfying $\sum_i v_i =$ 0 (vibrational ground state), 1 (fundamental tone states), and 2 (overtone and combination tone states). In addition to these states, we also considered states satisfying $2 + \sum_{i \neq 2} v_i = 3$, where the vibrational quantum number for C = O stretching mode (v_2) was constrained to be 2.

The vibrational averaged PAs for vibrational ground state (gs), fundamental tone, and overtone states are listed in Table II (the values for combination tone states are given in the Supplemental Material [42]). The excitations of modes 2 (C = O stretching), 3 (CH_2 bending), and 6 (CH_2 rocking) tend to enhance the vibrational PA values, while those of modes 1 (symmetric C–H stretching), 4 (out-of-plane bending), and 5 (antisymmetric C–H stretching) tend to decrease them. Among all vibrational modes, the C = O stretching mode gives the largest contribution to the enhancement of PA value, and the PA_v values are 30.69(6) meV for the fundamental tone state (2_1) and 36.07(8) meV overtone state (2_2). The PA values of 2_1 and 2_2 states are about 19% [4.91(7) meV] and 40% [10.29(9) meV] larger than that of the vibrational ground state, respectively.

We discuss here the relation between our theoretical PA values and the recent experimental ones which are evaluated as the energy difference between the peaks of VFR and IR spectra [8]. Assuming that their experimental PA values are the binding energy of a positron at the vibrational excited state of a molecule, our theoretical vibrational averaged PA values directly correspond to their experimental ones. Since the different vibrational states give different PA values as shown in Table II, the expected VFR shift for the CH_2O molecule should be different for each IR absorption peak. For the fundamental vibrational excitations of three modes having high IR intensities, the amount of VFR peak shifts from IR absorption peak of the C = O stretching, symmetric C–H stretching, and antisymmetric C–H stretching modes should be observed at about 30, 25, and 24 meV, respectively.

TABLE II. The vibrational averaged PA values of CH_2O molecule at the vibrational ground (gs), fundamental tone (X_1), and overtone (X_2) states. The absolute value of dipole moment (μ_v) and isotropic polarizability ($\alpha_{\mathrm{iso},v}$) at each state are also shown. The vibrational averaged values at other states are given in the Supplemental Material [42].

v[a]	$\mathrm{PA}_v^{\mathrm{CH_2O}}$ (meV)	μ_v (D)	$\alpha_{\mathrm{iso},v}$ (Å^3)
gs	25.78(3)	2.80	2.46
1_1	24.51(2)	2.76	2.51
2_1	30.69(6)	2.83	2.48
3_1	26.03(3)	2.80	2.47
4_1	24.88(3)	2.77	2.47
5_1	23.60(2)	2.74	2.51
6_1	25.91(3)	2.80	2.47
1_2	23.57(2)	2.72	2.56
2_2	36.07(8)	2.86	2.50
3_2	26.06(4)	2.79	2.48
4_2	24.08(3)	2.75	2.48
5_2	21.43(1)	2.68	2.57
6_2	26.14(3)	2.80	2.48

[a] X denotes vibrational modes: Symmetric C–H stretching (1), C = O stretching (2), CH_2 bending (3), out-of-plane bending (4), antisymmetric C–H stretching (5), and CH_2 rocking (6). The subscript is the vibrational quantum number of the corresponding vibrational mode, and vibrational quantum numbers for other modes are zero.

In order to analyze the various averaged PA values at each vibrational excited state in detail, we also calculated the dipole moment ($\boldsymbol{\mu}_v$) and polarizability ($\boldsymbol{\alpha}_v$) of the CH_2O molecule. Table II lists the absolute vibrational averaged value of $\boldsymbol{\mu}_v$ and isotropic polarizability ($\alpha_{\mathrm{iso},v} = \mathrm{Tr}\{\boldsymbol{\alpha}_v\}/3$) for all vibrational states. These values were obtained by the same scheme for the vibrational averaged PA, except that the global surfaces of dipole moment and polarizability were calculated at the HF/6-31+G($3d2f$) level of calculation. Table II clearly indicates that the increase of dipole moment tends to increase the PA_v value, while the polarizability has a small contribution to the values. To clarify the quantitative relation between these molecular properties, we performed the linear regression analysis (LRA) for the PA_v values with both μ_v and $\alpha_{\mathrm{iso},v}$ using the least-squares technique (Fig. 2). The fitted result is $\mathrm{PA}(\mu_v, \alpha_{\mathrm{iso},v}) = 72.8(1.5\mu_v + 1.0\alpha_{\mathrm{iso},v} - 6.3)$, where the units of PA, μ_v, and $\alpha_{\mathrm{iso},v}$ are meV, debye, and cubic angstrom, respectively. The coefficient of determination (R^2) with this fitted function is 0.96, which means that the PA values of the CH_2O molecule at each vibrational state are sufficiently explained as a function of μ_v and $\alpha_{\mathrm{iso},v}$. In addition, the R^2 values with the LRA using only μ_v or $\alpha_{\mathrm{iso},v}$ is 0.79 or 0.01, respectively, which means that the correlation between the PA_v and μ_v is considerably greater than that between the PA_v and $\alpha_{\mathrm{iso},v}$. Thus we can conclude that the PA variation at each vibrational state mainly arises from the variation of the permanent dipole moments rather than dipole polarizabilities.

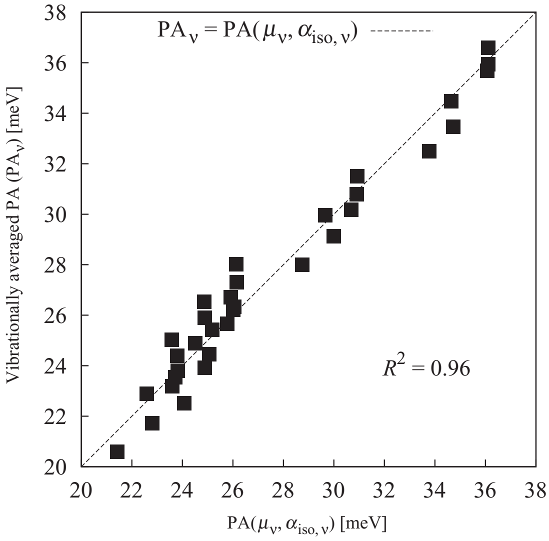

FIG. 2. The result of linear regression analysis for the vibrational averaged PA (PA_{ν}) values with dipole moment (μ_{ν}) and isotropic polarizability ($\alpha_{\mathrm{iso},\nu}$). The horizontal axis means the PA value estimated with the fitted function, $PA(\mu_{\nu},\alpha_{\mathrm{iso},\nu}) = 72.8(1.5\mu_{\nu}+1.0\alpha_{\mathrm{iso},\nu} - 6.3)$. The coefficient of determination (R^2) is also given.

Surko and co-workers [6] gave a similar equation for PA as $PA(\mu, \alpha, N_{\pi}) = 12.4(1.6\mu + 1.0\alpha + 2.4N_{\pi} - 5.6)$, where N_{π} denotes the number of π bonds for aromatic molecules and is zero for the CH_2O molecule. They have predicted the PA value of the CH_2O molecule as 11 meV from the above equation using experimental values of dipole moment (2.3 D) and polarizability (2.8 Å^3). Our vibrational averaged PA values for all vibrational modes are, however, more than twice their predicted value. Such discrepancy could be mainly due to our larger prefactor of 72.8 than that of their equation. It should be noted that the prefactor in their fitted equation was determined for various kinds of molecules, while our prefactor for only the CH_2O molecule. Thus, the difference in the prefactor would indicate that the contribution of dipole moment and polarizability to the PA value in the CH_2O molecule is greater than that in other molecules whose PA values are experimentally measured by them.

In summary, two types of PA values of CH_2O molecule are accurately calculated: (i) a *vertical* PA value at the equilibrium geometry, and (ii) a *vibrational averaged* PA value including anharmonic molecular vibrational effect. From the most accurate and reliable DMC calculation, the vertical PA value is calculated as +25(3) meV, which means that the CH_2O molecule is able to bind a positron at its equilibrium structure. To elucidate the effects of molecular vibrations on PA values, we also calculated vibrational averaged PA values with VSCF theory combined with CISD calculations having well-verified accuracy. The vibrational excitation of the C = O stretching mode gives the largest contribution to the PA enhancement in all vibrational modes, and the PA values at the fundamental and overtone states are about 31 and 36 meV, respectively. These results should help further development of experimental and theoretical study for positronic compounds.

The authors would like to thank Dr. R. J. Needs and Dr. M. D. Towler. Financial support was provided by Grant-in-Aid for Scientific Research and for the priority area by Ministry of Education, Culture, Sports, Science and Technology, Japan, for Y.K. and M.T.

---

[1] P. G. Coleman, *Positron Beams and Their Applications* (World Scientific, Singapore, 2000).
[2] M. Charlton and J. W. Humberston, *Positron Physics* (Cambridge University Press, Cambridge, UK, 2001).
[3] L. Sokoloff, M. Reivich, C. Kennedy, M. H. Des Rosiers, C. S. Patlak, K. D. Pettigrew, O. Sakurada, and M. Shinohara, J. Neurochem. **28**, 897 (1977).
[4] *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer Academic Publishers, The Netherlands, 2001).
[5] J. A. Young and C. M. Surko, Phys. Rev. A **78**, 032702 (2008).
[6] J. R. Danielson, J. A. Young, and C. M. Surko, J. Phys. B **42**, 235203 (2009).
[7] G. F. Gribakin, J. A. Young, and C. M. Surko, Rev. Mod. Phys. **82**, 2557 (2010).
[8] J. R. Danielson, J. J. Gosselin, and C. M. Surko, Phys. Rev. Lett. **104**, 233201 (2010).
[9] A. C. L. Jones, J. R. Danielson, J. J. Gosselin, M. R. Natisin, and C. M. Surko, New J. Phys. **14**, 015006 (2012).
[10] J. R. Danielson, A. C. L. Jones, M. R. Natisin, and C. M. Surko, Phys. Rev. Lett. **109**, 113201 (2012).
[11] P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).
[12] *Principles and Applications of Positron and Positronium Chemistry*, edited by Y. C. Jean, P. E. Mallone, and D. M. Schrader (World Scientific Publications, Singapore, 2003).
[13] J. N. Schoolery and A. H. Sharbaugh, Phys. Rev. **82**, 95 (1951).
[14] O. H. Crawford, Proc. Phys. Soc. **91**, 279 (1967).
[15] E. A. G. Armour, J.-M. Richard, and K. Varga, Phys. Rep. **413**, 1 (2005).
[16] K. Sato, K. Ito, K. Hirata, R. S. Yu, and Y. Kobayashi, Phys. Rev. B **71**, 012201 (2005).
[17] K. Sato, D. Shanai, Y. Hotani, T. Ougizawa, K. Ito, K. Hirata, and Y. Kobayashi, Phys. Rev. Lett. **96** 228302 (2006).
[18] K. Strasburger, Struct. Chem. **15**, 415 (2004).
[19] M. Tachikawa, Y. Kita, and R. J. Buenker, New J. Phys. **14**, 035004 (2012).
[20] A. Zecca, E. Trainotti, L. Chiari, G. García, F. Blanco, M. H. F. Bettega, M. T. do N. Varella, M. A. P. Lima, and M. J. Brunger, J. Phys. B **44**, 195202 (2011).
[21] D. Bressanini, M. Mella, and G. Morosi, J. Chem. Phys. **109**, 1716 (1998).
[22] M. Mella, G. Morosi, D. Bressanini, and S. Elli, J. Chem. Phys. **113**, 6154 (2000).
[23] M. Mella, D. Bressanini, and G. Morosi, J. Chem. Phys. **114**, 10579 (2001).
[24] Y. Kita, R. Maezono, M. Tachikawa, M. D. Towler, and R. J. Needs, J. Chem. Phys. **131**, 134310 (2009).
[25] Y. Kita, R. Maezono, M. Tachikawa, M. D. Towler, and R. J. Needs, J. Chem. Phys. **135**, 054108 (2011).

[26] K. Strasburger, J. Chem. Phys. **111**, 10555 (1999).
[27] J. Mitroy and G. G. Ryzhikh, J. Phys. B **33**, 3495 (2000).
[28] K. Strasburger, J. Chem. Phys. **114**, 615 (2001).
[29] J. Mitroy and J. Y. Zhang, Phys. Rev. A **83**, 064701 (2011).
[30] R. J. Needs, M. D. Towler, N. D. Drummond, and P. López Ríos, J. Phys.: Condens. Matter **22**, 023201 (2010).
[31] M. Tachikawa, K. Mori, K. Suzuki, and K. Iguchi, Int. J. Quantum Chem. **70**, 491 (1998).
[32] M. Tachikawa, K. Mori, H. Nakai, and K. Iguchi, Chem. Phys. Lett. **290**, 437 (1998).
[33] M. Tachikawa, Chem. Phys. Lett. **350**, 269 (2001).
[34] The aug-cc-pVTZ and $[12s9p3d2f]$ Gaussian-type functions (GTFs) for electronic and positronic basis sets. The exponent of positronic basis were ranging from 3.0×10^{-6} to 1.0 for s-type GTFs and from 1.0×10^{-4} to 1.0 for p-type GTFs. The other positronic polarized GTF exponents were 3.0×10^{-4}, 1.0×10^{-4}, and 3.0×10^{-3} for d-type, and 1.0×10^{-3} for f-type GTFs. This positronic basis set was constructed to yield converged PA at this level of theory.
[35] F. A. Gianturco, J. Franz, R. J. Buenker, H.-P. Liebermann, L. Pichl, J.-M. Rost, M. Tachikawa, and M. Kimura, Phys. Rev. A **73**, 022705 (2006).
[36] The 6-31+G$(3d2f)$ and $[12s8p6d2f]$ GTFs were used for electronic and positronic basis sets, respectively. These basis sets were constructed to give the PA evaluated by DMC calculation at equilibrium geometry of CH_2O, and the difference between PA by CISD and DMC calculations was 0.15 meV at this geometry.
[37] J. K. G. Watson, Mol. Phys. **15**, 479 (1968).
[38] S. Carter, S. J. Culik, and J. M. Bowman, J. Chem. Phys. **107**, 10458 (1997).
[39] J. M. Bowman, J. Chem. Phys. **68**, 608 (1978).
[40] J. Toulouse and C. J. Umrigar, J. Chem. Phys. **128**, 174101 (2008).
[41] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[42] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevA.89.062711 for the vibrational averaged PA values, dipole moment, and isotropic polarizability of CH_2O molecule at the combination tone states.